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THE

CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, F.R.S., &c.

VOLUME XCI.—1905.

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THE CHEMICAL NEWS.

VOLUME XCI.

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No. 2354.—JANUARY 6, 1905.

NOTE ON THE ELECTROLYTIC RECOVERY OF TIN.*

By F. GELSTHARP.

An experiment was made with an electrolyte of pure sodium hydrate in water, strength 10° Tw. (sp. gr. 1.05), temperature about 80° C., anode and cathode of tin plate, area $19\frac{1}{2}$ sq. c.m. (3 sq. in.), placed about $\frac{1}{4}$ c.m. ($1\frac{1}{2}$ in.) apart.

After switching on the current a small quantity of hydrogen gas was liberated at the cathode, and a little oxygen at the anode, gradually diminishing. The voltmeter stood at $3\frac{1}{2}$ volts, and the ammeter at $\frac{1}{2}$ ampère. The current was allowed to pass for about half an hour to see if the usual energetic electrolysis would commence; but no, the current continued to effect only a slight evolution of gas without stripping the tin from the anode. On examining the anode it was found to be very little attacked, but appeared to be covered with an extremely thin coat of a light brownish tint, which was not easily rubbed off. The current was again turned on without any different result.

The colouration was thought to be due to some low oxide of tin, which is a poor conductor of electricity. Therefore the effect of reducing it by means of hydrogen was tried, this being done by reversing the current for a moment. Then after reversing again the direction of the current the tin-plate anode was completely stripped of its coating of tin in a very few minutes, hydrogen gas being energetically liberated at the cathode, which also became coated with loose, spongy tin. While this reaction was going on the ammeter rose to $1\frac{1}{2}$ ampères, and the voltmeter fell to less than one volt, and when the cathode was agitated so as to knock against the sides of the containing vessel, the ammeter rose to two ampères, and the voltmeter fell to about half a volt.

Various pieces of tin-plate were tried under the same conditions, and it was noticed that the clean bright pieces acted in the same way as that just described; but pieces of old, oxidised, and tarnished tin-plate were attacked at once, and quickly stripped.

It was found that instead of reversing the current to make the reaction start, it could be brought about by placing in contact with the anode in the electrolyte for a short time a piece of clean iron, most effective being a piece of tin-plate which had just been stripped in the bath.

From the results of these experiments the writer conjectures, or suggests, that the clean, bright tin-plate (differing from tarnished or oxidised tin) at first becomes thinly coated with a black or brown oxide which is

insoluble in sodium hydrate, and that the effect of reversing the current, or making contact with iron, causes a deposit of hydrogen on the anode, which reduces this oxide to metal, thus roughening the surface, and making it in a favourable state for forming the soluble oxide, and when once the formation of soluble oxide has commenced, the electrolysis goes on uninterruptedly.

I bring this reaction before the Society in the hope that some member who may have investigated it will endeavour to give a satisfactory explanation of it.

After all the tin was stripped from the anode, the ammeter again fell to about half an ampère, the voltmeter rising to $2\frac{1}{2}$ volts; and when the current was continued the iron became coated with a reddish coloured deposit (probably composed of oxide of iron), which was not easily rubbed off.

I noticed that the deposited tin, when squeezed and placed in water, generated hydrogen gas. This evidently points to the fact that spongy tin deposited in a sodium hydrate electrolyte is not only an alloy of tin and hydrogen, but also contains some sodium.

The agitation of the cathode in a special way seems to be an important point so far as the consumption of electric energy is concerned. The resistance due to polarisation can be reduced to a minimum not only by moving the electrode vigorously and quick circulation of the electrolyte, but by giving it a quick succession of shocks produced by striking sharply. By this means the electric energy can be reduced by 30 to 40 per cent.

Comparing the acid and alkali processes for tin recovery, it is beyond doubt that the latter process is superior. In the alkali process iron apparatus may be used, and mechanical appliances for continuous treatment of tin-cuttings can be conveniently adapted; moreover, the electrolyte is continually being regenerated. In the acid process no suitable metallic apparatus can be used; therefore mechanical appliances are hardly admissible, and for the electrical treatment of tin-cuttings to be a commercial success they must be handled very cheaply. This can only be done by mechanical means with a continuous process.

For the manufacture of tin paste the acid is superior to the alkali process, as the deposited tin from the former is very light and amorphous, whilst that from the latter is much denser, and consists of minute crystals, which are not so suitable for the uses to which this material is put.

Society of Public Analysts.—A Meeting of the Society will be held on Wednesday, January 11th, 1905, at the Chemical Society's Rooms, Burlington House, Piccadilly, at 8 p.m., when a discussion on "Brandy" will be opened by Mr. Otto Hehner.

* A Paper read before the Faraday Society, December 19, 1904

THE ELECTROLYTIC FORMATION OF
COMPLEX CYANIDES.

By ANDRÉ BROCHET and JOSEPH PETIT.

WE have shown in a previous paper that platinum is easily soluble in the alkaline or alkaline-earth cyanides, under the influence of an alternating current, giving platino-cyanides.

Iron, which is equally insoluble in cyanides under the influence of a continuous current, behaves in the same manner as platinum with an alternating current.

Ferrocyanide of Potassium.—If we electrolyse a solution of cyanide of potassium by means of iron electrodes, using an alternating current, we observe at the same time an abundant disengagement of gas, and the solution of the electrodes with the formation of ferrocyanide, according to the equation:—



At the same time a thick froth is formed which eventually rises out of the vessel, while the hydrogen given off has a sickening odour, more or less intense according to the quality of the metal employed. This odour is also met with in the case of nickel and cobalt.

The variation of the density of the current has only a

pure, and on the other hand a portion of it is oxidised, giving carbonic acid gas and ammonia. There is no formation of ferricyanide; this latter being incompatible with cyanide of potassium.

The concentrated solution of ferrocyanide is cooled rapidly, the salt is drained by means of a filter-pump, washed with alcohol-water, and set to crystallise in water.

Cobaltcyanide of Potassium.—Cobalt behaves in the same manner as iron in the electrolysis of cyanide of potassium under the influence of an alternating current. Our experiments were again carried out on solutions containing 4 grm.-molecules per litre.

Contrary to what we have observed with iron, the density of the current has a certain effect, as in the case of copper, zinc, and nickel. The electrolyser was a vessel of rectangular section, cooled both on the inside and outside. The electrodes consisted of two strips of cobalt $6 \times 8.3 = 50$ square centimetres. The results obtained are given in Table III.

The amount of cobalt entering into solution in three experiments was 96, 98.6, and 100 per cent of the amount calculated from the cyanide of potassium. During the course of the experiments, the bright strips gradually became covered either with a black layer of oxide of cobalt, or with a rose-coloured precipitate, probably consisting of cobaltcyanide of cobalt, analogous to Prussian blue.

TABLE I.—Solution of Iron in Cyanide of Potassium. Influence of the Density of the Current.

Surface of the Electrodes, 40 sq. c.m.; Strength of Solution, 4 grm.-molecules per Litre.								
Temperature.	Intensity.		Time in minutes.	Density of current.	Iron dissolved.			Return, per cent.
	Eff.	Mean.			Found.	Calculated.	Per ampère-hour.	
	Ampères.	Ampères.						
15°	20.0	18	10	45	1.02	3.13	0.341	32.5
12°	11.1	10	30	25	1.53	5.22	0.306	29.3
11°	3.3	3	50	7.5	0.73	2.61	0.292	28.0
11°	1.45	1.3	120	3.25	0.67	2.72	0.258	24.7

TABLE II.—Influence of Temperature.

Surface of the Electrodes, 16 sq. c.m.; Strength of Solution, 4 grm.-molecules per Litre.								
Temperature.	Eff. Ampères.	Mean. Ampères.	Time in minutes.	Density of current.	Found. Grms.	Calculated. Grms.	Per ampère-hour. Grms.	Return, per cent.
23°	11.1	10	15	62.5	0.93	2.62	0.372	35.3
90°	11.1	10	30	62.5	2.87	5.23	0.575	55.0
100°	11.1	10	15	62.5	1.77	2.80	0.660	63.2

TABLE III.—Solution of Cobalt in Cyanide of Potassium. Influence of the Density of the Current.

Surface of the Electrodes, 50 sq. c.m.; Strength of Solution, 4 grm.-molecules per Litre.								
Temperature.	Eff. Ampères.	Mean. Ampères.	Time in minutes.	Density of current.	Found. Grms.	Calculated. Grms.	Per ampère-hour. Grms.	Return, per cent.
20°	20	18	15	36	3.27	4.95	0.728	68.3
15°	10	9	30	18	2.71	4.95	0.603	54.7
10°	5	4.5	60	9	2.05	4.95	0.457	41.4
12°	2.5	2.25	120	4.7	1.05	4.95	0.234	21.2

slight effect on the return, as shown by Table I. The experiments were carried out in a vessel of square section, cooled inside and out in the manner we described in the case of copper (*Bull. Soc. Chim.*, [3], 1904, vol. xxxi., p. 309).

Other experiments carried out with different apparatus have given analogous results, even when increasing the density of the current to more than 100 ampères per square decimetre.

The results obtained show that the solution takes place with a return corresponding to one-third of the calculated amount for densities of current varying within very considerable limits. The effect of temperature is much more marked, as is shown in Table II., which results were obtained in an apparatus, heated on the water-bath, with wires 5 m.m. in diameter.

All our experiments were carried out with a solution of cyanide containing 4 grm.-molecules per litre.

If we try to saturate the cyanide of potassium, we observe that the amount of iron entering into solution corresponds approximately with theory for the reaction I. In fact, we found 96, 91, and 91 per cent. Now the cyanide of potassium, on the one hand, was not perfectly

In our calculations of the return we assumed that the metal was dissolved in the cobaltous state, giving the corresponding salt, $\text{Co}(\text{CN})_2$, and consequently the cobaltocyanide, $\text{Co} + 6\text{KCN} + 2\text{H}_2\text{O} = \text{Co}(\text{CN})_6\text{K}_4 + 2\text{KOH} + \text{H}_2$.

This little known salt is very difficult to isolate on account of its energetic reducing action. It is oxidised rapidly in contact with the air, and even in contact with water it gives off hydrogen, especially if the liquid is warm. This is what takes place in the present case if the electrolyte is not kept very cold; we have observed, besides the disengagement of hydrogen at the electrodes, the formation of this same gas throughout the whole of the mass of the liquid. To avoid projections, it is more simple to prevent this spontaneous oxidation, and to transform the cobaltocyanide into cobaltcyanide in the ordinary way, which consists in passing a current of air through the solution.

We might oxidise the cobaltocyanide by means of electrolysis. With a current density of 5 ampères per square decimetre there is no formation of gas at the anode.

To collect the cobaltcyanide, $\text{Co}_2(\text{CN})_{12}\text{K}_6$, the solution is treated with acetic acid to destroy the alkali, the cyanide, and the carbonate, and then precipitated with alcohol.

This product is drained by means of the filter-pump, and set to crystallise in water.

Here we observe the opposite to that which we noticed in the case of iron. Not only is the cobaltcyanide compatible with cyanide of potassium, but the cobaltocyanide is oxidised spontaneously even in the presence of the latter salt.

Conclusions.—In a previous paper we showed that copper, as well as other metals such as zinc and nickel, are dissolved under the action of a sinusoidal alternating current, giving double cyanides.

In the present paper, and the preceding ones, we have established the fact that platinum, iron, and cobalt are also dissolved, giving double cyanides.

At first sight it appears as if the action of the alternating current is the same in both cases. But this is not so. In fact, copper may be precipitated, under the action of a continuous current, from the solution of its double cyanide, which behaves thus as a salt of copper from the electrolytic point of view.

Thus it appears that the metal is not combined in a complex ion in the true sense of the word, while in the ferrocyanide, for example, which behaves like a salt of potassium, we have a veritable complex ion from which it is impossible to separate the iron by means of electrolysis.

In both types of cyanide the metal forms a complex ion from the chemical point of view, but here again we know that the difference is very distinct between the two series.

The hypothesis of Le Blanc and Schick, according to which the solution of a metal under the influence of an alternating current is due to the formation of a complex ion, undecomposable by the current, does not apply in the case of copper, zinc, and nickel, as we have already proved. Does it apply to the case of iron or platinum? No better.

This hypothesis, in fact, assumes that the metal is soluble in a solution of cyanide when it is used as the anode; this is not the case.

The solution of platinum and iron under the influence of the alternating current should result, therefore, from a special action which we do not yet understand, but which we are engaged in following up.—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 12.

Action of Acetylene on Mercuric Chloride Solution.—Heinrich Biltz and Otto Mumm.—The authors lead acetylene through a 2.5 per cent solution of mercuric chloride for six to eight hours, washed the precipitate carefully with water, alcohol, and ether, and dried in the vacuum desiccator over sulphuric acid. The analysis of the product gave the formula $C_2HOHg_3Cl_3$ and quantitative syntheses conclusively prove that three molecules of mercuric chloride react with one molecule of acetylene to form trichloro mercuric acetaldehyde. In presence of one or two molecules of sodium chloride the same substance is formed, $C_2HHg_3Cl_5$, which is unstable towards water, being formed as an intermediate product. On shaking for a long time with chlorine water, the trichloro mercuric acetaldehyde yields a mixture of mercuric chloride and chloral. When iodine reacts with this substance in alcoholic or ethereal solution, two atoms of iodine are bound to every atom of mercury, but only half this quantity of iodine is taken up if a potassium iodide solution of iodine or iodine and water are used. No tri-iodo acetaldehyde or tri-iodo acetic acid or iodoform results, but all the iodine is bound to the mercury. But if iodine and sodium hydrate solution act simultaneously on the trichloro mercuric acetaldehyde, iodoform is produced.—*Berichte*, xxxvii., No. 16.

* The examination of the variation of frequency by utilising, as did Le Blanc and Schick, a series of currents alternately in the positive and the negative direction, will apparently give results quite different from those obtained with copper. If the platinum and the iron are dissolved, it is probable that the solution will tend towards zero both with a high frequency and with a low one, and that this solution will reach a maximum for a determined rate of frequency.

NOTE ON THE DETERMINATION OF CHROMIUM IN STEEL.

By F. IBBOTSON, B.Sc., and R. HOWDEN, B.Sc.

IN a paper on the volumetric estimation of manganese (*Journ. Chem. Soc.*, 1895, p. 277), Reddrop and Ramage state that in a solution containing nitric acid, a salt of chromium is very slowly but completely oxidised by sodium bismuthate to chromic acid. One of us and H. Brearley have pointed out (*CHEMICAL NEWS*, lxxxiv., p. 247) that the oxidation is so slow that the interference of the chromium with the determination of the manganese by this method is negligible.

Not infrequently the contingency arises of making a complete analysis of a steel on a very small amount of sample drillings, and it therefore seemed desirable to ascertain under what circumstances a determination of chromium could be obtained from the sample weighed off for a manganese determination. The authors have found the following method to yield satisfactory results.

After completing the manganese determination in the ordinary manner of titrating the permanganate filtered off after oxidation in the cold, of a nitric acid solution of the steel, by means of sodium bismuthate, about 50 c.c. of nitric acid of sp.gr. 1.20 are added along with 10 grms. of sodium bismuthate and the cold mixture is heated, without undue haste, up to boiling. The permanganate, which is regenerated on the addition of the bismuthate, assists in the oxidation of the chromium, and when the temperature reaches that of boiling, the oxidation is complete; the whole of the bismuthate is decomposed, and a clear red solution results. A pinch of manganous sulphate is now added and the boiling continued for a minute or two to decompose the permanganate. The precipitated manganic oxide, which is very small in amount and retains a trace only of the chromium, is then filtered off and the chromic acid in the filtrate, after dilution if necessary, determined in the usual manner by means of ferrous sulphate and a standard solution of potassium permanganate.

Metallurgical Department,
University College, Sheffield.

USE OF THE CHROMATES OF BARIUM AND OF SILVER IN THE DETERMINATION OF SULPHATES AND CHLORIDES.

By LAUNCELOT W. ANDREWS.

SEVERAL years ago a method was described by the author (*Am. Chem. Journ.*, 1889, xi., 567) for the volumetric determination of sulphates, of which the leading features may be recalled in outline here. A reagent, prepared by dissolving barium chromate in dilute hydrochloric acid, was added to the sulphate solution, the liquid was then neutralised, and, after filtration, the chromate in the filtrate titrated iodometrically in the usual manner. The amount of chromate so found was equivalent to the sulphate originally present.

This process is both accurate and rapid, as shown by my own observations, and those of others (Marchlewski, *Fres. Zeit.*, 1893, xxxii., 316; Reuter, *Chem. Zeitung*, 1898, xxii., 357; compare also Stolle, *Zeit. Angew. Chem.*, 1892, p. 234). It suffers, however, from a rather serious drawback, namely, that a solution of barium chromate in hydrochloric acid of the prescribed concentration does not keep perfectly (A. von Asboth, *Chem. Zeitung*, 1892, xvi., 922), a fact overlooked at the time of the publication of my first paper referred to above, owing to the fact that I had not then had occasion to work with solutions which had been kept more than ten days. Hydrochloric acid is, nevertheless, gradually oxidised by chromic acid, even in solutions far more dilute than the weakest which could be practically used for dissolving barium chromate, although weeks,

months, or years may be requisite to make the action very apparent.

To overcome this difficulty, which has doubtless stood in the way of a more general employment of the method in question, it is obviously necessary to substitute for the hydrochloric acid some other acid which will not be capable of oxidising by chromic acid, which will not itself be either an oxidising or a reducing agent in its action on hydriodic or chromic acids, and which will be sufficiently strong to dissolve the requisite amount of barium chromate. As possessing these qualifications two acids come into consideration in the first rank, *i.e.*, trichloroacetic and perchloric acids. The latter would probably be extremely well suited to the purpose, but it cannot, at present, be obtained by purchase in a sufficiently pure state; that is, free from hydrochloric acid and from all lower acids of chlorine.

Trichloroacetic acid meets all requirements as to resisting the action of chromic acid, and it can be purchased in the pure state without trouble. A normal solution of this acid is capable of dissolving the finely divided barium chromate rather freely, but not very rapidly. The solution may be aided by the application of gentle heat, but caution must be observed in this direction in order to avoid too extensive hydrolysis. Thus, a normal solution of trichloroacetic acid was agitated with an excess of barium chromate at about 90° for a few minutes, free evolution of carbon dioxide and chloroform occurring. The liquid was then cooled, and allowed to stand for three days at the temperature of the room.

A slight re-crystallisation of the barium chromate had taken place. The liquid now contained in each c.c. 126 m.grms. of trichloroacetic acid and 24 m.grms. of barium chromate. On further standing, an increased deposition of the chromate was observed. For practical purposes it may be assumed that in concentrations between normal and seminormal, trichloroacetic acid is capable of maintaining permanently in solution one-sixth of its own weight of barium chromate. Observations on this solution have now continued six months, and no change has been noted that in any way influences the analytical results obtained with it. Of course, the hydrolysis of the trichloroacetic acid goes on, but this change is slow and has absolutely no bearing, since the solution is not employed as a standard, and is always used in excess.

This modification entirely does away with the only objection to the method in its original form. No other change is required beyond the substitution of trichloroacetic for hydrochloric acid, so that for all details reference may be made to the former paper (*loc. cit.*).

Since the question of priority has been raised concerning the original method as between myself and Quantin, I desire to state what the facts are that bear on the history of the process. My method was described in a paper read before the Iowa Academy of Sciences in Des Moines, Dec. 27, 1887 (the proceedings of this meeting were not published till 1890), which was published in the *American Chemical Journal* in 1889 (*loc. cit.*). Quantin published in 1899 a somewhat similar process (*Bull. Soc. Chim.*, 1889, [3], i., 21), of which the following are the features:—Equal volumes of equivalent standard solutions of potassium dichromate and of barium chloride are mixed with sufficient hydrochloric acid to keep the barium chromate from separating. This liquid is added to the sulphate solution, then ammonia to alkaline reaction, and, after filtration, the chromate in solution is titrated by standardised ferrous sulphate, using potassium ferricyanide as indicator of the end of the reaction. Quantin had previously published practically the same method in 1886 (*Moniteur Scientifique*, 1886, p. 1222; also reprinted in *CHEMICAL NEWS*, liv., 233). It will be seen that Quantin's method differs from mine not only in the choice of titration by ferrous solution, but in the far more important particular that two or three* titrated solutions are demanded by this process, whereas only one is used in mine, because in the latter the proper

relation between barium and chromic acid is secured by starting with pure barium chromate instead of placing dependence upon a preliminary analytical process to secure this end. Hence the former method always demands a correction, variable in each case. Naturally, if I had been aware of Quantin's publications I would not have omitted to mention them, but at the time his second paper had not reached this country, and his first was not mentioned in publications available to me. As a matter of fact, the only points in common to the essentially different methods is that both make use of barium and of chromic acid salts.

It appears as if the principle, peculiar to my method, of using a re-precipitable salt is capable of more extended application, as, for instance, to the determination of chlorides. Thus, if silver chromate is added to a solution of a chloride, an equivalent amount of chromate passes into solution in accordance with the equation, $2\text{MCl} + \text{Ag}_2\text{CrO}_4 = \text{M}_2\text{CrO}_4 + 2\text{AgCl}$, and a colorimetric or volumetric titration of the chromate allows a conclusion as to the amount of the chloride, bromide, &c., originally present (compare De Koninck and Niboul, *Zeit. f. Analyt. Chem.*, 1891, p. 295). The feasibility of this scheme has been tested under my direction by Mr. H. V. Farr, who has obtained excellent results. A new volumetric method for determining chlorides is hardly a desideratum, perhaps, but a good colorimetric method for estimating traces of chlorides, as for example, in water analysis, cannot be regarded as superfluous. The experiments have demonstrated that it is not necessary to bring the silver chromate into solution by any acid. It is sufficient to agitate the finely divided and carefully prepared salt with the highly dilute chloride solution, then to filter or decant, and compare the depth of colour of the clear liquid with that of a suitable series of types made by dissolving known amounts of potassium monochromate in water. These type solutions keep indefinitely. The process is much more rapid than any titration method, and for the most dilute solutions is at least as accurate. It is expected to follow this preliminary notice of the method by a more detailed account.—*American Chemical Journal*, xxxii., No. 5.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, December 14th, 1904.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

MESSRS. J. C. Cain and W. H. Willcox were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. James Hector Barnes, B.Sc., The Briars, King's Norton, Birmingham; Bernard Mount Jones, B.A., "Alcala," Hermitage Road, Upper Norwood, S.E.; Herbert Louis Leech, 3, London Road, Blackburn; Alfred Courtenay Luck, The Naval Arsenal, Zarate, Argentina; Andrew Norman Meldrum, D.Sc., 16, Moorocks Road, Sheffield; Charles Watson Moore, B.Sc., 38, Demesne Road, Whalley Range, Manchester; Ernest Quant, 2, Park Crescent, Torquay; Gustav Arthur Troye, P.O. Box 2706, Johannesburg; William Phillip Want, 11, Pearfield Road, Forest Hill, S.E.; John Wells Wilkinson, M.A., 28, Egerton Terrace, Bexley Road, Belvedere; Alan Herbert Williams, 127, Roseneath Road, Urmston, near Manchester.

The following certificate was authorised by Council under By-law I. (3):—H. Chandra Chatterjee, Cawnpore, India.

Of the following papers, those marked * were read:—

*209. "Hydrolysis of Ammonium Salts." By VICTOR HERBERT VELEY.

* Two in the modified, three in the first process (1886)

When aqueous solutions of ammonium salts are heated to their boiling points, the evolution of ammonia and the concomitant acidity of the solutions result not from a direct dissociation, but from hydrolysis. Three cases are presented:—(i.) the hydrolysis is *nil* or inappreciable, (ii.) it is dependent on the dilution, and (iii.) it is independent of dilution when beyond a certain limiting value.

The persistence or avidity with which the several acids retain the ammonia in combination is analogous to their activity or avidity in the cases of hydrolysis of methyl acetate, and the inversion of cane-sugar, the relative, but not the absolute, order of magnitude being the same in all these three chemical changes.

DISCUSSION.

Prof. CROSSLEY said that this behaviour of ammonium salts on distillation was capable of being of great service in the separation of organic acids, and instanced the case (*Trans.*, 1898, lxxxiii., 13) where it had been found possible to separate isopropylsuccinic acid from a complicated mixture of fatty acids by distilling in steam a solution of the mixed acids in ammonium hydroxide, when ammonium isopropylsuccinate was left in the residue.

*210. "The Viscosity of Liquid Mixtures." (Part II.). By ALBERT ERNEST DUNSTAN.

The author's conclusions in a previous paper (*Trans.*, 1904, lxxxv., 817) are confirmed by the present series of results, and by means of a slightly modified apparatus the viscosity-concentration curves for the following mixtures have been investigated:—

1. Allyl alcohol and water:—Maximum point at 51–52 per cent allyl alcohol, corresponding with 1 allyl alcohol, 3 water, and a discontinuity with 40 per cent allyl alcohol corresponding with 1 allyl alcohol, 5 water.

2. Propyl alcohol and water:—Maximum point at 61–62 per cent propyl alcohol, corresponding with 1 propyl alcohol, 2 water.

3. Glycol and water:—Sagged curve approximating to the normal. Maximum divergence from the straight line at the point 1 glycol, 2 water.

4. Lactic acid and water:—Sagged curve as for glycol and water. Maximum divergence at the point 1 lactic acid, 2 water.

5. Benzene and acetic acid:—Minimum point at 89 per cent benzene, corresponding with 5 benzene, 1 acetic acid.

6. Benzene and propyl alcohol:—Minimum point at 95 per cent benzene, corresponding with 12 benzene, 1 propyl alcohol.

Although it might be expected that such very viscous substances as glycol and lactic acid, which at the same time are associative, would give maximum points in a similar way to other hydroxylated liquids, yet this is not the case, because further association or the formation of higher complexes with water is impossible; a breaking down into simpler groups takes place, although it is quite likely that aggregates are formed as in other cases.

The minima obtained with benzene solutions are regarded as being due to the formation of definite aggregates less complex than those of the original hydroxylated substances.

*211. "The Diazo-reaction in the Diphenyl Series. Part II. Ethoxybenzidine." By JOHN CANNELL CAIN.

The author has examined the action of heat on the solution of the diazonium salt prepared from ethoxybenzidine, and has shown that one diazonium group is normally substituted by hydroxyl, whilst the other remains intact. It seems certain from the fact that dianisidine is much more stable than benzidine in this connection that the diazonium group which is adjacent to the ethoxy-group is the one which remains unchanged. The diazonium sulphate has the formula $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_3(\text{OEt}) \cdot \text{N}(\text{N}) \cdot \text{HSO}_4$, and can be re-crystallised from boiling dilute sulphuric acid; it forms long acicular brown crystals easily soluble in water. The free diazonium hydroxide is precipitated by sodium carbonate as a lilac mass which dissolves in acids forming the corresponding salts.

4'-Hydroxy-3-ethoxydiphenyl-4-diazonium sulphate and the corresponding chloride, bromide, iodide, nitrate, and platinumchloride have been prepared.

*212. "The Sulphate and the Phosphate of the Dimercurammonium Series." By PRAFULLA CHANDRA RAY.

It has already been shown that when dimercurammonium nitrite, NHg_2NO_2 , is treated with a halogen acid the molecular structure of the compound is destroyed, and a double salt of the type $2\text{HgX}_2 \cdot \text{NH}_4\text{X}$ is formed, where X represents a halogen atom (*Trans.*, 1902, lxxxi., 644). If, however, an oxy-acid is substituted for the halogen acid, the dimercurammonium complex remains intact, and the NO_2 -group is simply replaced by the corresponding acid ion. In this way, the author has lately succeeded in preparing the sulphate, $(\text{NHg}_2)_2\text{SO}_4 \cdot 11\text{H}_2\text{O}$, and the phosphate, $\text{NHg}_2\text{H}_2\text{PO}_4$, of the series.

*213. "A Method for the Direct Production of certain Aminoazo-compounds." By RAPHAEL MELDOLA and LEWIS EYON.

The authors have found that most diazotised amines when treated in aqueous solution with a strong solution of sodium dichromate give crystalline precipitates of diazonium chromates which can be isolated and used in the solid condition. It is pointed out that this method is at present the only practical process for isolating diazonium salts with inorganic acid radicles from aqueous solutions. In the case of diamines, a means for the direct production of aminoazo-compounds has thus been found. Diazotised *p*-phenylenediamine gives a chromate having the formula $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{HCrO}_4$, which combines at once with phenols and amines to form aminoazo-compounds. *p*-Aminobenzeneazo-*B*-naphthol (*Trans.*, 1885, xlvii., 663) has been prepared by this method and characterised by its acetyl derivative, which crystallises in red needles melting at 259–260°. *p*-Aminophenol forms a normal diazonium dichromate, $[\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2]_2\text{Cr}_2\text{O}_7$. These solid chromates are all more or less explosive when dry, and it is suggested that some of them might find technical application as high explosives.

DISCUSSION.

Dr. HEWITT said that the much greater stability of *p*-aminophenyldiazonium salts as compared with salts not containing an amino-group may perhaps be accounted for by assuming that the former compounds have a quinonoid constitution. Professor Meldola's chromate would then have the formula $\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{HCrO}_4$, whilst the stable diazonium sulphate just described by Dr. Cain would have a similar formula, $\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_3(\text{OEt}) \cdot \text{N}_2 \cdot \text{H} \cdot \text{HSO}_4$.

Dr. CAIN inquired whether the diazonium chromate of *p*-nitroaniline had been prepared. It would be interesting to know whether this salt gave the ordinary "*p*-nitraniline red" on cloth padded with *B*-naphthol, or whether the chromic acid had any effect on the colour produced on the fibre.

Prof. MELDOLA, in reply to Dr. Cain, said that he had prepared diazonium chromates of the nitroanilines, but these substances were highly explosive when dry, and dangerous to make in quantity. In the moist state, they might perhaps be used for the purpose indicated. With reference to a question by Dr. Morgan, he had not been able to isolate chromates of the tetrazo-derivatives of simple diamines. With the heteronuclear diamines of the diphenyl series, it might be possible to obtain such tetrazonium chromates, but the experiments had not been carried very far in this direction at present. He agreed with Dr. Hewitt as to the remarkable stability of some of these diazonium chromates, but as to the inference that these salts might have a quinonoid structure on account of their colour, the fact that the acid radicle was itself coloured interfered with this interpretation, although there was no valid objection against such a view of their constitution.

*214. "The Combination of Mercaptans with Olefinic Ketonic Compounds." By SIEGFRIED RUHEMANN.

According to Posner's researches (*Ber.*, 1901, xxxiv.,

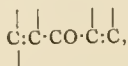
1395; 1902, xxxv., 799; 1904, xxxvii., 502). mercaptans generally interact with mono-olefinic ketones in the presence of hydrogen chloride, both by addition at the ethylene linking and by condensation with the ketonic group, to yield trithio-compounds.

The author showed that, on using piperidine or sodium ethoxide as catalytic agents, instead of hydrogen chloride, only additive products of mercaptans with the olefinic ketonic compounds—

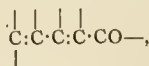


are formed, and several substances of this type have been obtained from benzylideneacetone, ethyl benzylideneacetate, benzylideneacetylacetone, and benzylidenebenzylacetone.

Moreover, in the presence of piperidine, dibenzylideneacetone, a diolefinic ketone containing the residue—



unites either with 1 or 2 molecular proportions of a mercaptan, whilst Posner, by means of hydrogen chloride, has only been able to obtain additive products with 2 mols. of mercaptans. On the other hand, cinnamylideneacetophenone, a ketone with the grouping—



takes up only one molecule of either isoamyl mercaptan or phenyl mercaptan; whilst according to Posner, this ketone, under the influence of hydrogen chloride, unites with 2 mols. of mercaptans. The author has, however, obtained from this ketone and phenyl mercaptan a compound identical with the substance described by Posner, but which has the formula $CHPh:CH \cdot CH(SPh) \cdot CH_2 \cdot C(Ph)_2$, and not $CHPh(SPh) \cdot CH_2 \cdot CH(SPh) \cdot CH_2 \cdot C(Ph)_2$, as stated by this investigator.

215. "Studies in Optical Superposition." (Part I.). By THOMAS STEWART PATTERSON and FRANCIS TAYLOR.

Menthyl acetate, *l*-menthyl *d*-tartrate, and *l*-menthyl diacetyl-*d*-tartrate have been prepared and their rotations examined between 0° and 100° and compared with each other, and with that of menthol between the same temperatures. Menthyl diacetyltartrate is dimorphous, one modification melting at 84.5° and the other at 108° . It is shown that for menthol there is a temperature ($58-59^\circ$) of minimum rotation (maximum negative rotation), but no such temperature has been observed for its derivatives. It is shown to be possible by analogy to trace the separate effects of the different active groups composing menthyl tartrate and its diacetyl derivative.

Wislicenus Memorial Lecture.

The Wislicenus Memorial Lecture will be delivered by Prof. W. H. PERKIN, F.R.S., on Wednesday, January 25, 1905, at 8.30 p.m.

THE FARADAY SOCIETY.

THE tenth Ordinary Meeting was held on Monday, December 19th, 1904, at the Institution of Electrical Engineers, Mr. J. SWINBURNE, Vice-President, occupying the chair.

The minutes of the November meeting having been confirmed and signed, the CHAIRMAN announced that the Council had made the following nominations of officers and members of Council to serve during the coming year. The election will take place at the annual general meeting, to be held in February.

President—Lord Kelvin, O.M.

Vice-Presidents—Prof. A. CRUM BROWN, F.R.S.; Sir W. HUGGINS, P.R.S.; Sir Oliver LODGE, F.R.S.; Dr. LUDWIG

MOND, F.R.S.; Lord RAYLEIGH, O.M.; Alex. SIEMENS, Pres.I.E.E.; James SWINBURNE.

Council—G. T. BEILBY, Bertram BLOUNT, W. R. COOPER, Sherard COWPER-COLES, Prof. A. K. HUNTINGTON, Dr. R. A. LEHFELDT, W. MURRAY MORRISON, Dr. W. S. SQUIRE, Dr. O. J. STEINHART, Prof. E. WILSON.

Treasurer—Dr. F. MOLLWO PERKIN.

THE CHAIRMAN then moved that Mr. L. GASTER and Dr. T. M. LOWRY be appointed auditors for the current year. The motion was carried unanimously.

M. ADOLPHE MINET communicated Part II. of his paper on "The Electric Furnace: its Origin, Transformations, and Applications," which was kindly read in abstract by Mr. R. S. HUTTON.

In the first and introductory part of his paper, which was read before the Society on June 9th last, M. Minet showed that the historical development of the electric furnace falls into the three following periods:—

1. Laboratory furnaces, 1808 to 1886.
2. Industrial furnaces, 1886 to 1890.
3. Development of industrial applications from 1890 to the present day.

The present instalment, after some preliminary general remarks on the E.M.F., current densities, and yields, with arc furnaces and resistance furnaces respectively, proceeds to deal in detail with the evolution of the furnace during the first period. The subject is sub-divided as follows:—

- (a). *Original furnaces*, namely, Davy's Arc, Pepys' resistance furnace for the cementation of iron, and Davy's and Napier's cathode furnace.
- (b). *Electrolysis at high temperatures*: the production of aluminium and its alloys, and the alkali and alkaline earth metals.
- (c). *Miscellaneous furnaces*, of which the most important are the early Despretz and Pichon furnaces, Berthelot's electric "egg" for the synthesis of acetylene, Siemens' and Huntington's well-known steel and other furnaces, the Louis Clerc furnace, interesting as the progenitor of the famous Moissan type, and Borchers' resistance furnace.

The paper, which is illustrated with diagrams of the principal furnaces alluded to in the text, closes with a bibliography covering the period dealt with. A final instalment will discuss the furnaces of the second and third periods.

Mr. W. B. CLARKE referred to the importance and difficulty of making temperature determinations of electric furnace processes, and expressed the hope that M. Minet would deal with that question in Part III. of his paper.

Mr. L. GASTA handed round some "siloxicon"—one of the newest products of the electric furnace—and described its properties.

Mr. E. KILBURN SCOTT (communicated) described some of his experiences in the early days of the manufacture of calcium carbide.

THE CHAIRMAN described a novel type of furnace that he had once hit upon by accident, and which he thought might turn out to be useful. He was sending a current through fused barium chloride, and the temperature having been allowed to get too high, the cast-iron crucible melted and formed a fused mass that was kept together by an outer skin of solidified chloride. This suggested the use of a neutral substance like barium chloride for heating to a very high temperature alloys or metals which it was desired not to contaminate with impurities.

Composition of Colloidal Granules.—Victor Henri and André Mayer.—The authors investigate the conditions of precipitation of colloid solutions. The particular case examined is the precipitation of copper ferrocyanide. They find that the proportion of FeC_6K_4 contained in the granules to that contained in the intergranular liquid diminishes in proportion as the quantity of FeC_6K_4 contained in the mixture increases.—C. R., cxxxix., No. 23.

NOTICES OF BOOKS

Guide to the Analysis of Potable Spirits. By S. ARCHIBALD VASEY, F.I.C., F.C.S. London: Baillière, Tindall, and Cox. 1904. Pp. 87.

The object of the present work is to induce analysts to take up a more detailed examination of potable spirits than has hitherto been the practice. Up to quite recently the only practical control over the sale of spirits has been the estimation of their alcoholic strength; under such a system it is obvious that whether the sample examined be brandy, gin, rum, or whisky, is quite immaterial.

The patent or fractionating still is practically the key to the situation as regards the analysis of potable spirits. By its use, as is well known, a strong, pure, and therefore featureless spirit is produced, free from any characteristic odour or flavour; on the other hand, the pot still yields a more or less impure spirit, partly owing to the formation of secondary products of fermentation, and partly because of bodies formed during distillation, which impart to it a characteristic odour and flavour according to the materials used.

It is evident that the pot-still cannot be dispensed with so long as the true flavour of brandy or whisky is looked for, this flavour arising from the presence of secondary products, among which may be reckoned compound ethers, volatile acids, aldehydes including furfural, and alcohols of the higher series, such as amylac and butylic alcohol.

Thus we see that a grain or *patent* spirit is free from, or contains a relatively small proportion of by-products, while a pot spirit contains these *impurities* in relatively large amounts. Thus it is easy to distinguish a pot spirit from a patent spirit by chemical analysis, and an analysis based upon an accurate determination of the secondary or by-products, gives a very fair indication of the nature of the spirit.

The book is divided into ten chapters, and in Chapter III. we commence with methods of analysis, standards, and the distillation of the spirit for analysis. Chapters IV. to VII. deal with the estimation of aldehydes and acids, the higher alcohols, the compound ethers, and furfural; Chapter VIII. is on the importance of taste, and in Chapter IX. we find the general considerations deduced from the results of analysis. Chapter X. is on colorimeters, and then follows the appendix, consisting of tables giving types of grain and root spirits, genuine whiskeys, brandies, rum, gin, and blended spirits.

The book is written and arranged in a very clear and concise manner, but would be improved by the addition of an index.

Gunpowder and Ammunition: Their Origin and Progress. By Lieut.-Colonel HENRY W. L. HIME, (late) Royal Artillery. London, New York, and Bombay: Longmans, Green, and Co. 1904. Pp. 256.

ONE of the principal ingredients of gunpowder is saltpetre, and therefore the invention of gunpowder was impossible until saltpetre was known. In attempting to fix the approximate date of the discovery of this salt, the author has made a careful search through old writings and records. No mention of saltpetre has been found anywhere before the thirteenth century. The Greek alchemists of preceding centuries are silent, and there is no saltpetre in the earliest recipe for Greek fire, ascribed to Marcus Græcusc, either in the Paris MSS. of 1300, or in the Munich MS. of 1438.

The Arab alchemists, before the thirteenth century, are as silent as the Greeks; there is no word for saltpetre about the middle of the thirteenth century, according to Romocki, and Friar Bacon, whose *De Secretis* was written before 1249, was thoroughly acquainted with the salt. The simple and very probable conclusion drawn from the fore-

going facts is, that saltpetre was not discovered until the second quarter of the thirteenth century, but this conclusion is not universally accepted, as some authorities hold that it had been used secretly by the Greeks for five hundred years previously. This latter theory is examined in Chapter III., and does not appear to have a very firm foundation. It is true that the earlier Greeks used a mixture called "sea-fire," which burned with much noise and vapour and was projected from syphons, but the author is of the opinion—and we think with good reason—that sea-fire was a mixture of sulphur, quicklime, and naphtha, in certain definite proportions.

It is very generally believed that the Chinese knew and made use of gunpowder in very remote times, but we are told here that no Chinese writer of repute upholds that idea; indeed, Chinese annals give no support to this hypothesis, and there does not appear to be any military evidence that the Chinese were in possession of an explosive in either the thirteenth or fourteenth centuries.

In Chapter VIII., on Friar Bacon, the author examines carefully the claims of this wonderful man, and finally concludes that if he did not *invent*, he at least *discovered* gunpowder; while experimenting with some incendiary composition prepared with pure saltpetre, the mixture exploded unexpectedly and shattered all the apparatus near it, thereby laying the foundation of the mediæval legend about the destruction of the Brazen head.

In Part II. of this volume we come to the more modern side of the subject, viz., the "Progress of Ammunition." In Chapter IX. ammunition is classified under its various heads, and in subsequent chapters these are dealt with separately; the principal classes into which the author divides ammunition, are—hand ammunition, war rockets, gunpowder, shock projectiles, igneous projectiles, igniters, and signals.

There are a number of tables, interspersed throughout the book, giving a good deal of interesting information as to the composition of various gunpowders, &c., at different periods, comparative costs of one round fired with shot of different materials, comparative pressure on the bore when firing shot of different materials, the composition of matches, time fuses, &c., at different periods, and other subjects.

The book is one of great interest and is written in an admirable style; besides its value to those engaged professionally with the subject, it can be cordially recommended to the general reader of scientific literature.

The book is well printed and is provided with an index.

Subject List of the Works on the Fine and Graphic Arts (including Photography), and Art Industries, in the Library of the Patent Office. London: Darling and Son. 1904. Pp. 374.

THIS subject list is a much larger one than any of its predecessors; it is divided into two parts—(a) a general alphabet of subject headings, with entries in chronological order of the works arranged under these headings; and (b) a key, or summary of these headings, shown in class order.

The present list comprises 2916 works (189 serials, 2727 text-books, &c.), representing some 5373 volumes. The catalogue entries relating to these works number 3645, and are distributed under 518 headings and sub-headings.

The Principles of Inorganic Chemistry. By WILHELM OSTWALD. Translated, with the Author's sanction, by ALEX. FINDLAY, M.A., Ph.D., D.Sc. Second Edition. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1904.

THE second edition of Prof. Ostwald's classical work was published in Germany at the beginning of this year, and is now followed by this second English edition, revised in accordance with the new German edition. A few altera-

tions have been rendered necessary in some branches of the subject, in which exceptionally rapid development has taken place. Thus the sections on the uranium rays and radio-activity have been entirely re-written specially for this translation by the translator, who is doing great service to the study of chemistry in this country in rendering Ostwald's valuable works accessible to English students.

The Electric Furnace. By HENRI MOISSAN. Translated by A. T. DI MOUTREFF, B.Sc. (Lond.), M.Sc. (Vict.), Ph.D. London: Edward Arnold. 1904.

THIS translation of Prof. Moissan's well-known work on the electric furnace, in which are described his researches on the volatilisation of refractory bodies and the preparation of some elements and binary compounds, includes the new matter contained in the German edition, and Prof. Moissan has also written a new chapter on some of the most recent work he has performed. This chapter, which of course adds considerably to the value of the English translation, describes work on the carbides of neodymium, praseodymium, and samarium. Silicides of vanadium and cerium, and borides of silicon, the properties of these new substances and their preparation being fully discussed. It is interesting to notice that the behaviour of the carbide of samarium shows this element to be more closely related to yttrium than to the cerium metals.

Metallurgy of Pig Iron, Wrought Iron, and Steel. By W. LIPIN, Professor in the Mining Institute of Catherine II. Volume I. 760 pages, with numerous illustrations. St. Petersburg. 1904.

PROF. LIPIN has published in Russian the first volume of his work, which may be called a very noteworthy experiment to produce an originally written book, as up to the present Russian metallurgical literature consisted mostly of translations of foreign books. Certainly the latter have been carefully consulted by the author when writing his book, and a list of them is given in the preface; but what is worth noting is that he never forgets to give examples from Russian metallurgical practice, together with drawings of Russian blast-furnaces, &c. This kind of information is generally rather meagre in other metallurgical publications.

Prof. Lipin has occupied for several years the post of chief metallurgist of the Pootiloff Works, St. Petersburg, where he has completed several important researches on the action of copper and molybdenum on iron and steel.

The volume just published contains—(I.) a very detailed description of the properties of iron, and of the action on this element of various other admixtures, and (II.) the production of pig-iron.

Salts and Their Reactions. By LEONARD DOBRIN, Ph.D., and HUGH MARSHALL, D.Sc., F.R.S. Edinburgh: James Thin. London: Simpkin, Marshall, and Co., Ltd. 1904.

PROF. CRUM BROWN, who contributes the preface, states that this book has developed from a series of notes drawn up originally for the benefit of a class of medical students, and that the object kept before the authors was to give such students a knowledge of the principles of chemistry, while at the same time providing them with a guide for use in the identification of salts in solution, with a view to enabling them to pass examinations. In pursuance of this object the nature and general properties of salts are discussed, and the theory of the behaviour of salts in solution presented from an ionic point of view to the student, who should thus have no excuse for being contented with a merely superficial knowledge of the commonest reactions of the various classes of compounds. Whether the average medical student would have the time to work through and digest all the matter contained in such a book is another question, but there can be no doubt that his knowledge of practical, and indeed of

theoretical, chemistry would be all the more firmly established if he did so. The authors have wisely included short sections on the theory of volumetric analysis, and might with advantage have given more practical examples. The notes on the strength of the solutions of the common reagents are highly commendable, as being likely to introduce as early as possible the idea of the quantitative relations obtaining between the various reagents in familiar reactions. The practical part of the book includes all the usual directions for detecting the more common ions, with a systematic and complete scheme for the detection of a single salt in solution. The appendix contains the reactions of the rare metals, and the examination of a substance in the dry way, and the book provides a useful course in practical chemistry and elementary qualitative analysis.

Chemisch-technische Untersuchungsmethoden. ("The Chemical Examination of Technical Products.") By Dr. GEORG LUNGE. Vol. II. Fifth Edition. Berlin: Julius Springer. 1904.

THE second volume of the new edition of Dr. Lunge's valuable work—the first volume of which appeared and was noticed in these columns a few months ago—begins with the analysis of iron and its ores and of metals other than iron, including such of their salts as are of technical importance. The examination of artificial manures of all descriptions is next treated, full details of the analysis of special varieties being given. Feeding substances, such as oil-cakes, meals, &c., are shortly discussed, and also various explosives; English regulations for heating tests, when they differ from those enforced on the Continent, being taken into consideration. The rest of the volume includes the chemistry of gas manufacture and the technical examination of coal-gas, the investigation of the by-products of this, as well as the coal-tar industry, and the technology of the inorganic dyes. In this volume Dr. Lunge is responsible only for the short section on carbide and acetylene, all the other sections being written by one or other of his collaborators, who in all cases possess special and sometimes unique qualifications for the tasks entrusted to them.

The Chemical Synthesis of Vital Products and the Interrelations between Organic Compounds. By RAPHAEL MELDOLA, F.R.S., V.P.C.S., F.I.C., &c. Vol. I. London: Edward Arnold. 1904.

IN a book of this kind the reader naturally turns with special interest to the preface, in which it may be expected that the author will express his views on the doctrines of vitalism and neovitalism, and this particular preface and introduction cannot fail to be read with great interest; it contains short articles on the history of organic chemical synthesis, the nature of the so-called vital products, the biocentric point of view as regards organic chemistry and chemical synthesis, and the advantages of the biocentric treatment of synthetical chemistry, all treated with the utmost caution and moderation, though there is no difficulty in deducing from them the author's own views. In the section on the history of organic chemical synthesis Prof. Meldola undoubtedly establishes Henry Hennell's claims to have synthesised a vital product—alcohol—at least as early as Wohler succeeded in preparing urea from ammonium cyanate. The term "vital product" is used in its very widest sense, and under it are included some compounds which may not be contained in the organism as such, but may have been formed from more or less complex molecules during or by reason of the process of extraction. The adoption of this wide definition has of course necessitated an enormous increase in the size of the book, but at the same time the author is quite justified in endeavouring to make the work as comprehensive as possible. In the sections on the biocentric standpoint it is specially interesting to read that the

general tendency of the work is to bring back carbon chemistry to the point from which it started when Wöhler first synthesised urea. The author states that at present the testimony of pure chemistry cannot logically be interpreted as a negation of the doctrine of vitalism, and warns the reader that the laboratory process is not by any means to be regarded as a reproduction of the process in the organism. Surprisingly little is known regarding the chemical evolution of any compound in the organism, and workers in this branch may find in the book some hints on this obscure subject. The text of this volume gives tabular statements of the natural sources, and synthetical preparation of various classes of organic compounds, compiled with the help of the best text-books on the subject and with constant reference to recent literature down to the end of the year 1902. An appendix contains some additional syntheses, especially in the camphor, terpene, and flavone groups, which have been accomplished during the printing of the volume.

CORRESPONDENCE.

HUNGARY AND BOHEMIA.

To the Editor of the Chemical News.

SIR.—In the CHEMICAL NEWS for November 18, 1904 (vol. xc., p. 255), I read:—"The French chemists were ignorant of the source of the ore from which they had discovered their radium, and were relying on the pitchblende products of the 'Hungarian' mines." To confound Hungary with Bohemia is a very frequent mistake of the English and French author. As a matter of fact, to confound the Bohemians with the Hungarians is as great a mistake as to confound the Russians with the Chinese. The Bohemians are Slavs (like Russians), the Hungarians are Mongols (like Chinese).

Jačymov (Joachimsthal, German), where the radium was found, is in the old kingdom of Bohemia—where Tcheques (Bohemians) are dwelling (Jean Hus, the follower of J. Wiclex, was a Tcheque)—and not in Hungary.

Hoping that you will kindly permit me to correct this mistake.—I am, &c.,

Prof. Dr. ALEXANDER BATEK.

Pízen, Bohemia, Klatovská třída c. 4.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxix., No. 23, December 5, 1904.

Action of Methylene Chloride and Aluminium Chloride on Toluene.—James Lavaux.—When methylene chloride and aluminium chloride react on toluene, the resulting products appear to be mixtures which can only be partially separated by solvents. In the product of this reaction, described by Friedel and Crafts as melting at 232°, the author finds two dimethylantracenes, A and B. A, being less soluble, can be isolated in a pure state from the mixture and melts at 240°. The other product, B, can only be obtained pure by transforming it into its dimethylantraquinone, which substance can be purified and melts at 244.5°. He also discovers, besides these two bodies, two other solid products: one, a third dimethylantracene (C), extremely soluble in all organic solvents, and which melts at 86°; the other, β -monomethyl anthracene. The two latter are present only in very small proportions.

Retrogradation of certain Secondary Cyclic Amines.—P. Lemoult.—The author examines the amines represented by the formula $R-N\begin{smallmatrix} \text{H} \\ \text{R} \end{smallmatrix}$. These give with PCl_3 and PCl_5 volatile products, amongst which the body $R'Cl$ is found. There is therefore a retrogradation of a secondary amine into aniline, which is very noticeable in the case of PCl_5 and monomethylaniline, and maintained—though more obscure—in the other cases. He noticed the first reaction of this kind. Benzoyl chloride, when acted upon by dimethyl- and diethylaniline, gives the bodies $C_{11}H_7Cl$ and $C_{12}H_{11}Cl$. More recently Auger extended this reaction to the chlorides of the fatty acids; it only takes place, in the cases known up to the present time, on the tertiary amines. The secondary amines undergo, with $R-COCl$, regular acylation.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxvii., No. 16, 1904.

Stereochemistry of Chromium.—P. Pfeiffer.—The author has succeeded in preparing several series of isomeric chromium salts, and has shown that the behaviour of the isomers can only be explained by one interpretation of the phenomena exhibited. He has discovered, moreover, interesting relations between chromium and cobalt salts, by which Werner's configuration formulae of stereo-isomeric cobalt salts are confirmed. The chromium salts in question are all simply-constituted addition products of trivalent chromium salts and ethylene diamine, corresponding to the empirical formula, $CrX_3 + 2en$, where en is an abbreviation for ethylene diamine. Their constitution is given by the formula $(en_2CrX_2)X$, according to Werner's theory, by which one negative residue, X , possesses an ionic character, while the other two, and also the en molecule, are closely bound to the chromium atom. The compound $(en_2Cr(SCN)_2)SCN$ exists both in the form of long needles (the α -form), and also as small orange glittering scales (the β -form). These are not examples of dimorphism, but are undoubtedly two chemically isomeric individuals, for from them can be prepared a whole series of salts (chloride, bromide, nitrate, &c.), which differ in crystalline form, and also in colour, solubility, and chemical reactions. The effect of oxidation shows that both series are normal rhodanate compounds possessing the structural formula $(en_2Cr \begin{smallmatrix} S.CN \\ S.CN \end{smallmatrix})X$, and are structurally identical. The rhodanate residue can be replaced by other negative residues without destroying the isomerism; thus this residue does not contain the cause of the isomerism. Also the author obtained another series of isomeric compounds of essentially simpler composition than the first. If the α -dirhodanate rhodanide, after being made pasty with water, is treated with chlorine, a chloride of formula $(en_2CrCl_2)Cl$ is formed, and from this a series of green salts can be prepared of general formula $(en_2CrCl_2)X$. The two intra-radical chlorine atoms possess no ionic character, for on dissolving the nitrate in water no chloride reaction is at first obtained with silver nitrate, though by degrees a turbidity, and finally a precipitate appears. From the second, or β -series of dirhodanate rhodanide salts, a series of violet salts can be prepared similarly. By the transpositions of the oxalic derivatives of di-ethylene diamine chromic salts, $(en_2CrC_2O_4)X$, it may be shown that the β -rhodanate salts and the violet dichloro salts belong to the "cis" form, while the green dichloro salts and the α -dirhodanate salts are "trans" compounds. The one form may be readily converted into the other as follows:—If the aqueous solution of a green dichloro salt be allowed to stand for some days, the colour changes to red, and on evaporation with hydrochloric acid a residue is obtained from which a considerable quantity of the isomeric violet dichloro chloride can be isolated. If the aqueous solution of the violet salt is repeatedly evaporated with addition of hydrochloric acid and mercury silver chloride and the residue is taken up

with water, a green crystalline powder remains behind, which is the mercury silver chloride double salt of the green trans-dichloro chloride. The analogous cobalt salts exist also in two isomeric forms, which differ in colour, being green (trans) and violet (cis) respectively.

Quantitative Determination of Ammonia and Amides.—J. Effront.—In studying the reaction of ammonia and amides with hypochlorites, the author came to the following conclusions:—1. An alkaline solution of hypochlorite can be kept in absence of air in daylight for about thirty hours without losing chlorine. 2. The amides, imides, nitril bases, acid amides, and amido acids react at ordinary temperatures on hypochlorite, a loss of bleaching chlorine taking place; this loss is in direct proportion to the weight of the organic substance used. 3. The ammonium bases at the ordinary temperature give no reaction with hypochlorite. The fact that the quantity of chlorine set free is in direct proportion to the weight of the substance used can be used to determine the above nitrogen compounds by means of a solution of arsenious acid. Twenty c.c. of a solution of bleaching powder (containing 1.5 to 2 per cent of chlorine), 20 c.c. of normal sodium hydrate, and 1 to 5 c.c. of a 1 per cent solution of the substance to be examined, are introduced into a flask which is filled with distilled water, closed, and kept in the dark for twelve to fifteen hours. For the chlorine determination a solution of arsenious acid is used, the excess of the acid being titrated back by means of an iodine solution. Thus from the quantities of chlorine found the reduction value of the substance used is obtained. This method of determining ammonia is specially suited for water analysis. The reaction proceeds according to the following equation:— $2\text{NH}_3 + 3\text{CaOCl}_2 = 3\text{CaCl}_2 + 3\text{H}_2\text{O} + 2\text{N}$, the chlorine, per gram of ammonia being found = 6.55, and calculated = 6.258. In determining the ammonia in water the protein substances must be taken into account, as they possess a very high reduction value, which is constant for different protein substances, and may be used for their quantitative determination. The decomposition products of the protein substances have a lower reduction value than the natural albuminous substances. The effect of protein substances on the hypochlorite solution is only very slow, and the chlorine must not be determined within fourteen or sixteen hours from the beginning of the experiment.

A Colourless Chlorhydrate of Rosaniline.—Rudolf Lambrecht and Hugo Weil.—If ordinary crystalline rosaniline is dissolved in about two parts by volume of 30 per cent hydrochloric acid, crystals separate out from the liquid, which on washing with hydrochloric acid and drying in the vacuum desiccator over lime, are quite colourless. Similar crystals again separate from the mother-liquor on standing. They dissolve in water, giving a faintly pink solution. On heating the intense red colour of the fuchsine salts appears. Rosaniline base separates out on addition of alkalis to these solutions. Analysis shows the formula to be approximately $\text{C}_{20}\text{H}_{21}\text{N}_3\text{O} \cdot 2\text{HCl} + 4\text{H}_2\text{O}$. Thus colourless salts of rosaniline exist which have not three but only two molecules of HCl. Neufuchsine on similar treatment gives no crystals, even on standing for days.

Hydrates of Titanium Trihaloid Salts.—Arthur Stähler.—In its trivalent compounds titanium behaves like vanadium and chromium. Thus it may be conjectured that in vanadium and titanium trichloride an isomerism exists similar to that existing between the violet (grey-blue) and green $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ described by Werner as hydrate isomerism. Twenty-eight years ago Glatzel isolated from the hydrochloric acid solution of titanium a green substance to which he gave the formula $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$. Five years ago Polidori obtained a violet salt, $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$, by electrolytic reduction of the tetra-chloride. The author, in spite of repeated attempts, could not get Glatzel's green chloride. The concentrated solution of the violet trichloride became green on the addition of alcohol and

hydrochloric acid. This liquid gave no crystals of a green hydrate. But on addition of rubidium or caesium chloride to it, fairly stable double salts could be isolated, of composition $\text{TiCl}_3\text{Cs}_2 \cdot \text{H}_2\text{O}$ or $\text{TiCl}_3\text{Rb}_2 \cdot \text{H}_2\text{O}$. They separate in a pure condition only from the hot solution, and are decomposed by water, giving a violet solution. The chromium chloride salts of Neumann behave similarly, except that they were violet, giving a green solution in water. According to Werner, their structure was $(\text{Cr} < \text{Cl}_5 / \text{H}_2\text{O})\text{Rb}_2$. Chromium chloride also forms a series of green double salts which exist in the cold, and dissolve in water without change. These are represented by the formula $(\text{Cr} < \text{Cl}_2 / (\text{OH}_2)_4) \cdot 2\text{H}_2\text{O}$. The author has not obtained green titanium salts of this type, though similar violet salts seem to exist, or at any rate, from violet titanium chloride by addition of caesium chloride in the cold, violet double salts were formed which have approximately the composition $\text{TiCl}_3\text{Cs}_{2.4}\text{H}_2\text{O}$, but which cannot be isolated quite pure. By determining the chlorine which could be precipitated and the lowering of the freezing-point it was found that, as regards dissociation, the violet titanium chloride agrees very well with the violet chromium chloride. The author has prepared by the electrolytic reduction of the tetra-bromide and the tetra-iodide the hydrates of the tri-haloid salts, which are violet, and have the composition $\text{TiBr}_3 \cdot 6\text{H}_2\text{O}$ and $\text{TiI}_3 \cdot 6\text{H}_2\text{O}$. They are both less stable than the chloride, the bromide being more stable than the iodide. The bromide may be kept for a day *in vacuo* with only slight loss of weight, while the iodide in a shorter time becomes green, giving off water and hydriodic acid.

Red Compounds of Vanadium Trichloride Hydrate.—Arthur Stähler.—By dissolving $\text{VdCl}_3 \cdot 6\text{H}_2\text{O}$ (prepared electrolytically) and rubidium chloride in water, and evaporating on the water-bath, hydrochloric acid being introduced, raspberry-red crystals begin to separate out. These on analysis corresponded to the formula $\text{VdCl}_3\text{Rb}_2 \cdot \text{H}_2\text{O}$. The salt is difficultly soluble in water and alcohol, and gradually changes in water, giving a green solution. Corresponding compounds of ammonium, potassium, caesium, and magnesium are also red, and possess the same properties.

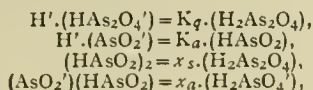
MISCELLANEOUS.

Electrolysis of Fused Chloride of Lead: Influence of the Density of the Current on the Returns.—A. Appelberg.—When electrolysing chloride of lead in an ordinary U-tube the return of lead diminishes regularly with the intensity of the current. With currents of great intensity (0.5 to 2 amperes for example), the variation observed in the return is slight; but this variation becomes very great with less densities of current. By prolonging the curve constructed, by taking for the axis of x the intensities, and for the axis of y the returns, this curve cuts the axis of x , not at the point $x=0$ but at a point $x=a$. At this strength the intensity of the current corresponds to a minimum tension, variable according to the conditions of the experiment, and with it the return is *nil*. The polarisation remains practically constant with high current densities, with lower densities the maximum of polarisation is not reached and varies with the density of the current. An examination of the anodic return shows that for high current densities the return of chlorine corresponds to the return of lead. With lower densities, we observe slight divergencies resulting apparently from the different conditions under which the experiments were carried out. By doing the electrolysis in straight or inclined cylindrical vessels, we get analogous results; in any case the return decreases much more rapidly as the

current density becomes smaller. The electrolysis of a eutectic mixture of chloride of lead and chloride of potassium does not give a cloudy deposit of lead like the electrolysis of pure PbCl_2 . Through the diminution of the solubility of lead in the saline mixture, and the possibility of operating at a lower temperature, Faraday's law is approximately verified with high intensities. The variation of the return with regard to the density of the current is always regular, but much slower than with pure chloride of lead. The electrolysis of the eutectic mixture of $\text{PbCl}_2 + n\text{NaCl}$ proceeds in a similar manner to that of the potassic mixture. The addition of chloride of iron (Fe_2Cl_6) to the mixture diminishes the return, and the loss of return is the greater as the proportion of iron is higher. The curves of return obtained may be represented by Lorentz's

formula, $a = 100 - \frac{K}{i^n}$; in which a = the return per cent, K and n = two constants, which can be easily calculated, and i the density of the current used.—*Zeit. Anorg. Chem.*, vol. xxxvi., p. 36.

Boric and Arsenious Acids: Study of the Formation of Complex Acids.—Friedrich Auerbach.—Arsenious acid is soluble in amyl alcohol. By shaking up the aqueous solution of this acid with amyl alcohol a portion of the acid goes into the alcohol. The coefficient of division between the alcohol and the water is 1:5.47. The addition of an excess of arsenious acid to a solution of arsenious ions, causes the formation of diarsenious monobasic ions, and probably still more complex ions. Further, the reaction is limited. The tendency to the formation of complex bodies is not very great, for at 25°, in the presence of an excess of 0.2 normal solution of arsenious acid, more than half the salt still remains in the state of monoarsenite. The diarsenious acid is a stronger one than monoarsenious acid, but, in the free state it can only exist in a very dilute solution. The constant of electrolytic dissociation of this complex, bimolecular acid, is to the co-efficient of dissociation of the monomolecular acid, as the constant of decomposition of the complex of the acid is to that of the anion; or, in other terms, by stating—



we get—

$$\frac{K_q}{K_a} = \frac{x_s}{x_a}$$

With boric acid we observe the same formation of complexes; but here the tendency is much more accentuated, for even in the presence of a very slight excess of acid, the solution only contains a very small percentage of monoborate. The type of the complex obtained depends on the concentration of the boric acid. Further, the polyboric acids are stronger acids than boric and monoarsenious acids, but in the free state, at a low temperature, they can only exist in very dilute solutions. By adding to a solution containing boric and arsenious acids a quantity of soda too small for saturation, we obtain very complex equilibria between the two monomolecular acids, the complex acids and their salts. The ratio $\frac{\text{total borate}}{\text{total arsenite}}$ is no longer proportional to the two simple acids, but depends, on the contrary, according to the law of masses, on the different complex acids which are formed.—*Zeit. Anorg. Chem.*, vol. xxxvii., p. 353.

MEETINGS FOR THE WEEK.

MONDAY, 9th.—Society of Chemical Industry, 8. "Some Chemical Aspects of the St. Louis Exhibition," by Walter F. Reid.

WEDNESDAY, 11th.—Society of Public Analysts, 8. Mr. Otto Hehner will open a Discussion on "Brandy."

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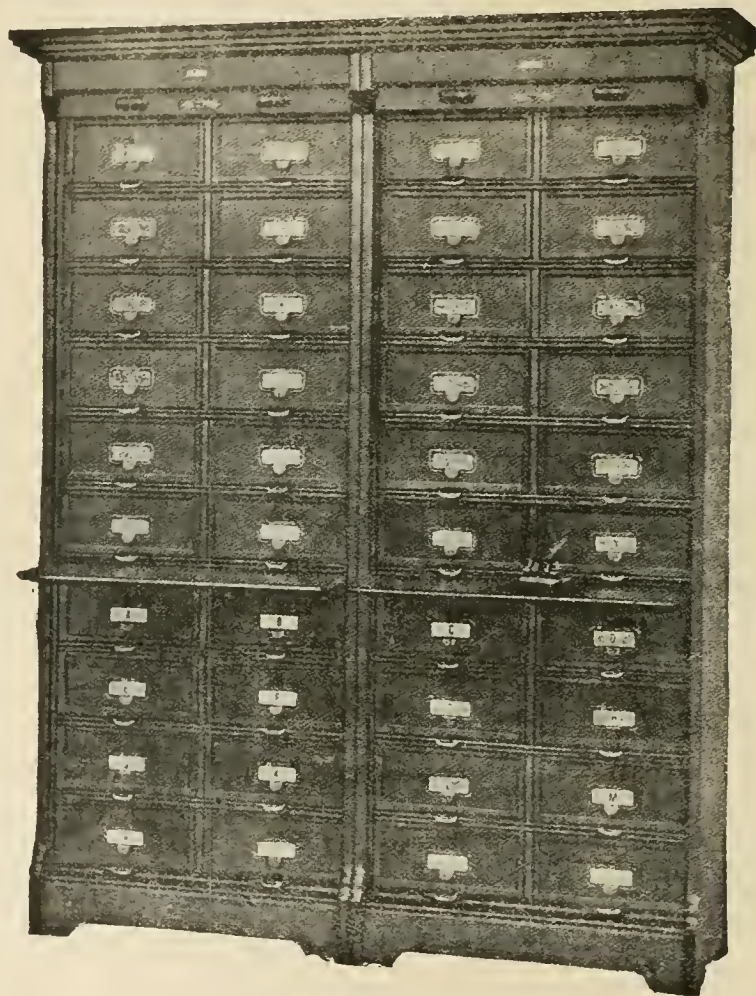
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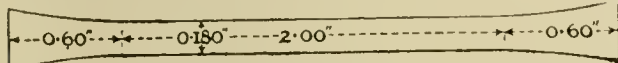
THE EFFECT OF LIQUID AIR TEMPERATURES ON THE MECHANICAL AND OTHER PROPERTIES OF IRON AND ITS ALLOYS.*

By Sir JAMES DEWAR, F.R.S., Hon. M.I.C.E.,

and
ROBERT ASHOLT HADFIELD, M.I.C.E.,
President-elect Iron and Steel Institute.

As many iron alloys have shown anomalous results in their physical behaviour at ordinary temperatures, it became advisable to ascertain the exact effect of very low temperatures upon such bodies, and, accordingly, a series of tests were carried out on standard iron and iron alloyed with other elements, the specimens being selected from a large collection made by one of the authors, which is located at the Hecla Works, Sheffield. In the course of the inquiry some 500 specimens have been examined, and the detailed description of each test will appear later on in a special Monograph. In the meantime the more important results are submitted to the Royal Society.

For the purpose of the experiments, the irons were taken in the form of forged bars, and the iron alloys in the form of cast ingots 2½ in. square. They were then carefully heated to the required forging temperatures and reduced to rods ½ in. diameter, and from these rods finished test-bars 0.180 in. diameter were accurately machined to the following sketch:—



The bars were then forwarded to the Royal Institution Laboratory, and there tested in a small hydraulic testing machine, similar in principle to that described in *Proceedings of the Royal Institution*, 1894, to which the necessary arrangements could be applied for breaking the specimens while immersed in liquid air.

The present research confirms, in a larger field, the conclusions set forth in the discourse of one of the authors at the Royal Institution, in 1894, on the "Scientific Uses of Liquid Air," in which the results of tests on metallic wires and cast metals at low temperatures were discussed. The results of the present series of tests corroborate the inference previously drawn, viz., that all common metals and alloys increase in tenacity at low temperatures, and this whether the ductility increases or decreases, and, further, that the increase of tenacity is solely due to the low temperature, and persists only during its continuance.

The Results of Low Temperatures on Irons.—The first specimen examined in this class was Swedish charcoal iron, this material in its composition most nearly approaching that of pure iron. The analysis of this specimen gave C 0.045, Si 0.07, S 0.005, P 0.004, Mn trace, Fe 99.82 per cent. This iron, after careful annealing, gave 20 tons per sq. in. tenacity and 20 per cent elongation at normal temperature; after cooling in liquid air the tenacity rose to 38 tons, with substantially no elongation. Another specimen, after being quenched at 950° C., and again at 600° C. in water, showed similar results in liquid air. Two other specimens in the unannealed condition and one after special heat treatment, showed similar properties. Specimens immersed in liquid air and allowed to return to the normal temperature before testing, showed almost exactly the same tenacity and elongation as before cooling, showing that the brittleness is entirely a function of temperature.

Several specimens were then quenched from 600° C., 800° C., and 950° C. in liquid air, and allowed to return to the normal temperature before testing. It might have been expected that with this extraordinary chilling a considerable hardening effect would have been noticed, but singular to say, whilst the tenacity is practically the same in each case, the ductility is improved rather than reduced. It may be mentioned that the specimens quenched from high temperatures in liquid air remained red-hot in the liquid air much longer than would have been expected. In order to determine the hardness of these Swedish charcoal irons, a series of tests were carried out by the Brinell ball test, which showed that the hardness is increased nearly 200 per cent by quenching in liquid air. The specimens, though, no doubt, much stiffer than at normal temperature, could be readily filed at -182° C. Magnetic tests also showed that no marked change takes place at low temperature as regards this quality.

In order to determine whether there is a critical point where the abnormal rise in tenacity and loss of ductility occurred, four specimens were tested at +18° C., -80° C., -100° C., and -193° C. respectively. The results clearly show that there is no critical point, i.e., gradual decrease in temperature is accompanied by gradual increase in tenacity.

Other irons tested were L.S.S. Swedish iron, English Bowling, and Cooke iron, all showing increase in tenacity and corresponding decrease in ductility upon quenching in liquid air.

The next class are *Iron-Carbon Alloys*. This class is of special interest and importance, as upon the various percentages of carbon present in steel depend chiefly its physical properties. The specimen in which manganese is absent, or present in only very small quantities (C 0.14,

Si 0.08, Mn 0.07 per cent), represents very mild or soft steel; it enables a comparison to be drawn between the Swedish charcoal iron, previously described, and soft steel. In the case of this specimen the tenacity was nearly trebled,

but it is apparently more ductile than Swedish charcoal iron. A specimen containing (C 0.78 per cent) showed a considerable rise in tenacity in liquid air, the ductility being reduced to practically nil. A specimen of the same material was also submitted to the liquid air temperature, and allowed to return to normal temperature before testing: it showed a similar result to the original specimen not so treated.

It may, therefore, be said that the effect produced by liquid air is of a physical and temporary character. Other specimens, viz., Nos. 115 (C 0.83, Mn 0.25 per cent), 9 (C 0.85, Mn 0.32 per cent), 10 (C 0.09, Mn 0.32 per cent), 13 (C 1.23, Mn 0.14 per cent) showed the usual behaviour at liquid air temperature. Specimens of No. 115 (C 0.83 per cent) were then quenched in liquid air from 700° C. and 750° C. respectively, and tested at normal temperature. As with the Swedish charcoal iron, the quenching from these comparatively high points has not produced the effect that might be expected; in fact, instead of the ductility being reduced, it is now quite considerable, viz., 13 per cent from the 700° C. and 8 per cent from the 750° C. Specimens of No. 13 (C 1.23 per cent) also showed the same singular effects after quenching from 700° C. and 750° C. in liquid air. It is certainly most remarkable that a specimen containing 1½ per cent C, suddenly lowered 930° C., is so little injured as regards ductility. If these specimens had been quenched from the same condition in ordinary water or oil, they would have been unfileable and of extraordinary hardness. These specimens were as magnetic at -182° C. as at normal temperature, and readily fileable.

In connection with this series, specimens were also taken of various iron-carbon alloys in which the Mn percentage was higher than in the preceding specimens, e.g., Test No. 110 (C 0.19, Mn 0.52 per cent), 1 (C 0.20, Mn 0.50 per cent), 2 (C 0.50, Mn 1.00 per cent), 3 (C 0.58, Mn 0.58 per cent), 5 (C 0.75, Mn 1.00 per cent), 11 (C 0.05,

* A Paper read before the Royal Society, December 8, 1904.

Mn 0.58 per cent), 12 (C 0.20, Mn 0.62 per cent), 31 (C 0.68, Mn 1.11 per cent). All these specimens showed the usual rise in tenacity and fall in ductility, and although Specimen No. 31 is of abnormally high carbon, yet this does not appear to have interfered with the ordinary effect of the liquid air treatment. In the case of Test No. 1, after quenching specimens of the same material in liquid air from 700° C. and 750° C., the same peculiar behaviour was noticed as previously described, *i.e.*, considerable increase in ductility.

Having now dealt with the iron-carbon alloys, the various other alloys may be dealt with:—

<i>Iron and Silicon</i>	{ Specimens were tested representing all these alloys, but the results do not call for any special comment, the usual increase in tenacity and fall in ductility being noticeable at low temperature.
<i>Iron and Aluminium</i>	
<i>Iron and Tungsten</i>	
<i>Iron and Chromium</i>	
<i>Iron and Copper</i>	

Iron and Nickel.—Specimen No. 45 (C 0.26, Ni 0.58 per cent). Although the liquid air doubles the tenacity, probably owing to the lower carbon and the presence of nickel, the elongation is not reduced to the extent noticed in previous specimens. This is important, and gives material proof that the brittleness of iron at low temperatures can be modified by another element, provided the carbon is not present in any considerable percentage. In another specimen, No. 46 (C 0.14, Ni 1.92 per cent), the nickel appears to vigorously assert itself, as the ductility at -182° C. only decreases from 20—12 per cent, the tenacity increasing from 34—59 tons. In Specimens Nos. 49 (C 0.19, Ni 3.82 per cent) and 50 (C 0.18, Ni 11.39 per cent), the remarkable effect of nickel is noticeable, as, whilst the tenacity rises considerably in both cases, the ductility remains practically unaltered. The tenacity rose in a further specimen, No. 54 (C 0.16, Ni 24.51 per cent), in which the nickel is very high, from 90—118 tons at -182° C., the ductility being only reduced from 12—10 per cent. The specimens were non-magnetic both at normal and at liquid air temperature. The same material showed an increase of from 306—524 in hardness under the liquid air treatment.

Iron and Manganese.—These form an important class. The peculiar alloy of iron and manganese known as "Manganese Steel" is non-magnetic, and it is possible to produce similar alloys of iron and manganese even when the former element is present in as high a proportion as 87—88 per cent. Excellent results as regards physical properties can be obtained upon exceeding 14 and up to 24 per cent, provided the carbon is low. From about 3—7 per cent the material is comparatively brittle, even with low carbon. Upon exceeding 7 per cent the material now known as "Era" manganese steel, is formed, and continues up to 17 or 18 per cent. Manganese steel proper is the alloy containing 11—15 per cent of manganese with carbon varying from 0.80—1.40 per cent.

We will deal first with manganese steels having low carbon, *i.e.*, under 0.30 per cent. Test No. 14 (C 0.08, Mn 3.50 per cent), the usual rise in tenacity and loss in ductility occurs at -182° C., and on the specimen being allowed to return to normal temperature it does not appear to be injured in any way. Samples Nos. 15, 16, and 17 (Mn varying from 5.40—15.28 per cent), which are extremely brittle at normal temperature, show very little modification at the low temperature.

Dealing now with alloys having higher percentages of carbon, several specimens tested with Mn ranging from 2.23 to 11.53 per cent, with carbon increasing proportionately from 0.41—1.66 per cent, showed normal behaviour at low temperature. An interesting specimen No. 26 (C 0.23, Mn 12.64 per cent) was examined, representing a normal "Hadfield manganese steel." At normal temperature this gave 56 tons tenacity, with the high elongation of 30 per cent, and after immersion in liquid air showed a slight rise in tenacity, the elongation, however, falling to 24 per cent, the low temperature thus entirely de-toughening the material. This result is some-

what unexpected, as it might have been anticipated that the great ductility of this material at normal temperature would not have been interfered with to any great extent at the low temperature. In the ordinary treatment of Mn steel for toughening, the sudden drop in temperature is about 1000° C., and in the liquid air only 200° C. A repetition test, No. 26A, gave a similar result, the tenacity at normal temperature being 65 tons, with 40 per cent elongation, while at -182° C. the ductility dropped to nil, the tenacity remaining the same, *viz.*, 64 tons.* Similar specimens of this steel cooled down and allowed to return to normal temperature again exhibited the usual extraordinary toughness of the material, thus showing that the de-toughening or embrittling action is only temporary, as with the Swedish charcoal iron and ordinary steel specimens.

It is certainly curious to find that a specimen of steel, which only a few moments before would break in the easiest manner, can again be bent double. This is produced by a change in temperature conditions of about 200° C. These results also show that manganese steel, notwithstanding its many peculiarities, in this respect falls into line with and is subject to the same laws as iron and ordinary steels. It is therefore all the more curious that the iron-nickel-manganese alloy (1414B) described later, entirely differs in this respect, where the effect of low temperature is not only nil, but there is a positive increase in ductility. The Ball tests on specimen No. 26 shows an increase in hardness at -182° C. of 70 per cent, *viz.*, from 205 to 372. Three other specimens, Nos. 26 E, F, and G, are also interesting as showing the effect of quenching upon Mn steel, from temperatures of 605°, 800°, and 950° C. in liquid air, the tests being then carried out at normal temperatures. The specimens E and F give similar results to those that would be obtained by quenching in ordinary cold water at 600° and 800° C., *i.e.*, little or no increase in ductility. On the other hand, in specimen 26 G, quenched from 950° C., there is no doubt the result obtained, 66 tons tenacity with 38 per cent elongation, is excellent, but it is not any better than can be obtained by quenching in water at 15° C. It is important to here mention that the three specimens E, F, G, were all non-magnetic at -182° C., showing that there is no change in the magnetic properties of manganese steel at low temperatures. This experiment finally settles quite a number of misunderstandings in metallurgical literature which have arisen on this subject, namely, that at no range of increase or decrease in temperature (provided this is not, as regards high temperature, sustained for any length of time) does any marked change in magnetic property occur in manganese steel.

The effect of low temperature on *Iron alloyed with Two other Main Elements.* Taking first the alloys of *Iron, Nickel, and Chromium.* Tests Nos. 78 (C 0.25, Cr 0.64, Ni 2.67 per cent) and 81 (C 0.89, Cr 2.00, Ni 1.92 per cent).—In the first instance in the presence of low carbon the nickel shows its toughening influence, as at -182° C. the tenacity rises from 38 to 61 tons, the elongation only falling from 20—17 per cent. In the latter specimen the effects of the nickel are not so apparent owing to the higher carbon, but the elongation does not entirely disappear. Another specimen of this latter material after quenching in oil at 760° C., and then water at 650° C., showed an increase in tenacity at -182° C. of from 81—105 tons, the elongation being, however, reduced from 74 per cent to nil. The embrittling influence of the carbon is seen in both instances. In the next specimen, No. 79 (C 0.31, Cr 1.80, Ni 2.60 per cent), the ductility is not effected, remaining at 15 per cent. Notwithstanding the considerable presence of chromium, the nickel asserts itself in this specimen, the tenacity rising from 49—79 tons. A similar result was also noticeable in specimen No. 107

* It is very extraordinary that the metal iron, no matter what its treatment, never becomes so ductile as the treated and quenched manganese steel—mainly composed of iron—with an original ductility of 40 per cent.

(C 1.17, Cr 1.55, Ni 3.02 per cent), the tenacity rising to 59 tons, and the ductility dropping only from 25—20 per cent. Test No. 80 (C 0.64, Cr 2.01, Ni 12.24 per cent).—In this specimen the very high tenacity at the normal temperature (115 tons) does not appear to be affected by the liquid air; in other words, a steel having high tenacity at normal temperature is practically unaffected by liquid air.

Iron, Nickel, and Silicon
Iron, Manganese, and Chromium

Iron, Manganese, and Silicon

Iron, Chromium, and Aluminium

Iron, Chromium, Silicon

Iron, Chromium, Copper

Iron, Chromium, and Tungsten

Tests were carried out in liquid air on specimens representing these alloys, but the results do not call for any special comment, in all cases the specimens behaving in the normal manner, i.e., showing increase in tenacity and decrease in ductility in liquid air.

Iron, Manganese, Copper.—Test No. 19 (C 0.25, Mn 2.01, Cu 1.39 per cent) shows a remarkable rise in tenacity, the elongation remaining unaffected by the low temperature. It is remarkable that the copper, which is present only to the extent of 1½ per cent, absolutely neutralises what would be the action of manganese, which clearly produces brittleness and hardness at low temperatures.

Iron, Cobalt, Manganese, Silicon

Iron, Chromium, Manganese, Silicon

Iron, Nickel, Manganese, Aluminium

Tests were carried out on specimens representing these alloys, but the results do not call for any special comment.

Iron, Nickel, and Manganese.—In this class a number of specially interesting results were obtained. There is an important alloy, No. 1109D (C 0.60, Mn 5.04, Ni 14.55 per cent), including two elements in exactly the same proportions, which, if added separately to iron, would cause extreme brittleness. Most singular to say, this double combination now confers extraordinary toughness. This alloy is probably the most ductile form of iron alloy known, in several cases an elongation of no less than 75 per cent having been obtained at normal temperature. Taking the first specimen, No. 60, under liquid air treatment, this material drops in elongation from 70—25 per cent, this remaining ductility even now being very great. This is the first specimen met with in which the ductility remains comparatively high. A further test carried out on the same steel shows a similar result. It may be mentioned that the magnetic qualities of the specimen remained unchanged at -182°C . 1109D may be termed almost non-magnetic, though not so much so as manganese steel. 1109D is much more sensitive to magnetic changes by temperature, though to an ordinary magnetic test it appears inert.

The next specimen, No. 61 (C 1.00, Mn 6.05, Ni 17.91 per cent), shows a further increase in nickel percentage, and this is clearly the factor in preventing loss of ductility at -182°C ., the ductility only decreasing from 57—42 per cent. Another specimen taken, No. 114 (C 1.18, Mn 6.05, Ni 24.30 per cent) shows a still further increase in percentage of nickel. For the first time in this series of tests there is now met with a specimen in which there is an actual rise in ductility at -182°C . The tenacity now rises from 51—84 tons, and the ductility from 60—to 67 per cent. This is remarkable. It is curious that the considerable percentage of manganese does not interfere with the toughening of the iron, of which there is 68 per cent. In any case it cannot be claimed that manganese confers this, as it must be remembered that a similar percentage of manganese in an iron alloy containing no nickel shows remarkable brittleness either at normal or low temperature. Nor does an iron alloy containing a similar high percentage of nickel and no manganese show much ductility. In face of these apparent anomalies it is

difficult to offer a satisfactory explanation of the remarkable effects noticed. A repetition of the above test showed even more remarkable results, the ductility rising from 42—57 per cent.

The liquid air experiments on this series (iron, nickel, manganese) bring out in a much clearer manner than any other tests have yet done, the remarkable toughness and ductility of the iron alloys containing 6 per cent Mn and 14—24 per cent nickel. They show what an extraordinary molecular combination has been produced. In other words, these particular iron alloys have almost non-magnetic properties, possess the highest electrical resistance of any known alloy, and also represent the most ductile iron alloy yet known.

The Concluding Group includes Metals and Miscellaneous Alloys.—The first specimen taken in this group was No. 120 forged nickel (C 0.09, Ni 99.27 per cent), representing an excellent quality of commercial nickel. This was tested in the forged condition, and in liquid air the tenacity was increased from 29—46 tons, and ductility from 43—51 per cent. This may be considered a remarkable result, and probably explains why in iron-nickel and iron-nickel-manganese alloys the presence of nickel (provided the carbon is low) prevents low temperature injuring iron. It is difficult to explain why this should be so, in view of the similar position of these two elements in the chemical classification of the elements.

Although no absolutely pure specimen of the metal manganese is yet available, that containing about 98 per cent shows comparative brittleness, and in this respect, therefore, entirely differs from the metal nickel. This, to some extent, explains why nickel-iron alloys are remarkably tough, but still leaves unsolved why manganese steel which contains 12 per cent of Mn, is so extraordinarily tough when alloyed with iron and some carbon, and quenched from high temperatures.

Test No. 131 (copper 99 per cent) shows that whilst the results obtained from this metal resemble nickel, the tenacity being increased, it is to a much less degree, the ductility not being materially altered.

It is curious to find that by chilling down the metals iron, nickel, and copper to -182°C . their absolute and ultimate—if the terms may be allowed—qualities are shown more truly than at the normal temperature. The effects here noticed also explain in a more satisfactory manner than has yet been possible, why nickel is so valuable in nickel-iron alloys; that is, it tends to counteract the constant tendency of the sensitive metal, iron, to become embrittled on the slightest provocation. If this research reveals this one important fact, it will have well repaid the labour.

From the results it would seem to be indicated that copper might be a useful metal to alloy with iron. There are, however, difficulties in the way of this, at any rate as regards forged metal, as copper-iron alloys containing no manganese are considerably red-short, and cannot be readily manipulated. For some reason not yet explained it also does not alloy well with iron, but this may be a question of temperature effect at fusion point. At any rate, these experiments are suggestive for further research and investigation.

In the case of aluminium, Test No. 113 (Al 99.50 per cent), the metal shows a remarkable increase in tenacity, viz., 8 to 15 tons, the elongation being nearly quadrupled, viz., from 7 to 27 per cent. Singularly enough, when alloyed with iron, such increases in both tenacity and ductility are not noticed; in fact, a contrary effect was produced.

Specimens of cupro-nickel (Cu 95, Ni 4.85 per cent) and Bull's metal showed only slight changes at low temperature, whilst specimens of delta metal and manganese copper showed a rise in tenacity and ductility.

Various experiments carried out in connection with this research deal with contraction, electrical properties, micro-structure, magnetic and brittleness tests, all of which will be included in the special monograph.

General Conclusions.

It is clear that as regards iron and iron alloys, with, however, certain exceptions, the effect of low temperature is to increase in a remarkable degree its maximum tensile stress, and to reduce its ductility to practically nothing. These changes take place to the same extent, and this is very curious in the softest wrought iron, as represented by the specimens S.C.I. (Swedish charcoal iron), L.S.S. (the famous Swedish melting iron), and also English wrought iron, and in carbon steel samples from 0.10 to 0.20 per cent to the high percentages, such as 1.25 or 1.50 per cent. Thus, the absence or presence of carbon in ordinary carbon steel, in which other special elements are not present, seems to have but little influence. That there is no error in this statement is proved, independently of the tensile tests, by the fact that several bars of the S.C.I., and mild steel specimens, were submitted to the low temperature test, and tested by hammer immediately after being immersed. In all cases they exhibited great brittleness, breaking off instantly upon being struck. Further confirmation is obtained by the Brinell hardness ball test, under which test the hardness number of the S.C.I. increased at -182°C . from 90 to 266, or about equal to the hardness of 0.80 per cent carbon steel at normal temperature. This almost seems almost incredible when it is remembered that the S.C.I. shows by analysis 99.88 per cent of iron, and has only 20 to 22 tons tenacity, with 25.30 per cent elongation.

The importance of the discovery of the toughening effect of nickel upon iron at low temperatures will be seen when it is understood that, whilst it has been well known that nickel in certain percentages produced important improvements in the qualities and properties of iron and steel alloys, no microscopical or chemical research work has yet proved why this came about. It seems clear that these experiments go a long way towards offering a satisfactory explanation. The experiments prove that the purest iron, as represented by the S.C.I. (containing 99.82 per cent iron), becomes brittle to an extraordinary degree under the influence of low temperatures; whereas nickel itself, tested under the same conditions, has improved rather than deteriorated, not only in tenacity, which iron also does, but in ductility, in which latter quality iron entirely breaks down. If nickel, therefore, is present in an iron alloy containing but little carbon, or comparatively low in that element, it acts as a preventive of brittleness, or is a very considerable modifier of that objectionable quality. It may be interesting to state that at ordinary temperatures the toughness or ductility of nickel is no greater than that of iron. For example, in comparative tensile tests made on nickel and pure iron, the ductility of iron was greater.

Iron to a more or less degree, at any rate in manufacturing operations, always seems to be endeavouring to wander out of the "paths" of ductility and toughness, and will assume its apparently brittle nature on the slightest provocation. It would appear, therefore, that iron, a cheap and convenient metal itself, must be permeated by some element that will mask or modify its properties. Until recently carbon was the only element known to modify the properties of iron; but, as will be seen in this research, this element, where great toughness is required, only helps to make matters worse. Fortunately for iron, however, its close companion nickel, acts as a preventive in keeping it from wandering out of the narrow road of metallurgical rectitude, that is toughness and ductility. Why this should be so cannot at present be explained. Iron is a crystalline metal, whereas nickel appears to be much more amorphous; it is possible, therefore, that nickel tends to prevent iron crystallising. This action of nickel is remarkable in certain of the alloy specimens, *e.g.*, No. 114, which is an alloy of iron, carbon 1.18 per cent, nickel 24.30 per cent, and manganese 6.05 per cent. Here the ductility is extraordinary at not only normal but low temperatures, probably the highest known

for any known iron alloy, and certainly for an alloy having such tenacity as 85 tons per sq. in. There is still present in this alloy 68 per cent of iron, yet the tendency of the latter metal to become brittle is not only entirely checked at the low temperature, but the elongation, already so great, is considerably increased, *viz.*, from 60 to 67½ per cent. There is also an increase of tenacity in both cases, *viz.*, a rise from 10 to 38 per cent. Thus the nickel present causes the bar under high tension, and at -182°C ., to remain far more ductile than the very best ductile iron of one-third the tenacity. Although the action of nickel has been specially referred to, it must not be overlooked that in this alloy there is also present 6 per cent of manganese, which in its ordinary combination with iron, that is with no nickel present, would confer intense brittleness upon the iron and render it more brittle than if not present. This treble combination of nickel, manganese, and iron, appears to reverse all the known laws of iron alloys.

We have to thank the mechanician of the Davy-Faraday Laboratory, Mr. C. N. Cooke, for able assistance in the conduct of the experiments.

ON THE
LUMINIFEROUS ETHER AS AN ELEMENT.

By WILLIAM ACKROYD, F.I.C., &c.

In 1902, I made an attempt to prove (the first such attempt, I believe) that the distribution of the elements in the universe bears an inverse relation to their atomic weights in comparable periodic groups (CHEMICAL NEWS, 1902, LXXXVII., 187). Thus the probable distribution of the halogens in the earth in per cent of its mass was shown to be as follows:—Chlorine, 4.8×10^{-4} ; bromine, 5.8×10^{-6} ; iodine, 5.8×10^{-8} . Fluorine with the lowest atomic weight is probably an exception so far as this planet is concerned. In 1903, figures were given by Sir William Ramsay which show that argon, krypton, and xenon conform to the law. Here, again, however, it is probable that helium and neon with the lightest atoms in their group will prove exceptions. In connection with these and other exceptions among the lightest elements, it must be remembered that the relative densities of the planets are as follows:—

Mercury	1.24
Venus	0.90
Earth	1.00
Mars	0.96
Jupiter	0.20
Saturn	0.12
Uranus	0.18
Neptune	0.17

With decreasing atomic weight among the elements we have decreasing density; therefore it necessarily follows that in the evolution of the planets the outer and lighter ones may have an excess of those elements which are wanting in requisite quantity on the earth to make them conform to the law.

The subject has acquired new interest in view of Mendeleeff's recent hypothesis that the luminiferous ether is an element. He places it in the helium family as having in extreme degree that inertness which characterises helium, neon, argon, krypton, and xenon, which he terms the zero group. He gives it an atomic weight immensely below the unity of hydrogen to explain its wide distribution in defiance of gravity. It is a matter of some interest to note that the low atomic weight assigned to it would make it the most plentiful element in its group in conformity with the relations which have been set forth, and it would evidently also have the unique distinction of being the most plentiful of all the elements in the universe.

ESTIMATION OF GLYCERIN IN RESIDUARY SOAP-LYES.

By R. FANTO.

SOME time ago, in collaboration with M. Zeisel, I published a new method for the estimation of glycerin, of which the simplicity and accuracy had been proved on triacetine and aqueous solutions of glycerin (*Zeit. f. Landw. Versuch. Oesterr.*, vol. v., p. 1902; *Zeit. f. Anal. Ch.*, vol. x., p. 636). Latterly we have shown that the same method could be employed for the estimation of glycerin in wines.

In the present note we propose to show that this method is applicable also to the estimation of glycerin in the residuary lyes from soap-making.

Knowing the composition of this kind of liquors, there was no fear that they would contain anything beyond the alkaline sulphates that might exercise any influence on the results of the estimation. The presence of even relatively large quantities of salts—iodide of potassium, acetate of soda, acetate of baryta, &c.—had no effect on the progress or the result of the estimation. It was hardly to be expected that chloride of sodium, which is the predominant salt in residuary lyes, would behave differently. Nevertheless, I thought it advisable to make several estimations of glycerin in the presence of chloride of sodium.

To a solution of glycerin, of which three portions of 5 c.c. each gave in three estimations 0.2447, 0.2444, and 0.2450 gram. of iodide of silver, and which contained consequently 1.92 per cent of glycerin, I added 3 per cent of pure chloride of sodium; 5 c.c. of this mixture gave 0.2428 gram. of AgI, corresponding to 1.91 per cent of glycerin. The same solution of glycerin, treated with 10 per cent of chloride of sodium, gave 0.2410 gram. of AgI; that is to say, 1.89 per cent of glycerin.

We see from these experiments that chloride of sodium exercises a certain influence on the result, but that the error is practically negligible. I have not examined more closely into the cause of this influence. It may be attributed probably to the formation of small quantities of chlorhydrine of which a portion is subjected to the action of the hydriodic acid, causing a slight loss of iodide of silver.

There remained for me to try the effect of the other substances contained in the residuary lyes from the point of view of their influence on the result of the estimation of glycerin. The firm of F. A. Jargs, Sohn, and Cie., of Leising, were good enough to supply me with a certain quantity of residuary soap-lye, with which I was enabled to try the following experiments:—

It was a yellowish brown, cloudy, slightly alkaline liquid. The analysis of the filtered liquid disclosed the presence of 0.63 per cent of Na_2SO_4 and 0.86 per cent of Na_2CO_3 . Five c.c. of the lye evaporated to dryness and calcined gave a residue of 0.3881 gram., or 7.76 per cent. The proportion of chloride of sodium was determined (a) in the residue, and (b) in 5 c.c. of the liquid diluted with five times its volume of water. The amount of chloride of silver obtained was:—(a) 0.8197, (b) 0.8222; mean, 0.8209 gram. AgCl, or 6.69 per cent of chloride of sodium.

The lye did not contain any volatile substances, and gave iodide of silver in my apparatus.

It was also necessary to determine whether the substance that gave the lye its brown colour had any effect on the result. For this purpose 20 c.c. of lye were treated with 180 c.c. of absolute alcohol; the mixture was left for a certain time, and filtered. The flocculent precipitate was washed at the bottom of the filter with absolute alcohol. The filtrate and the alcoholic washings were perfectly colourless. The precipitate was dissolved in water, and the solution obtained was diluted up to 100 c.c.; the sulphuric acid present was eliminated by means of acetate of baryta, the solution was evaporated down to 30 c.c. to drive off the alcohol, and then treated with 20 c.c. of water. Five c.c. of the yellow solution obtained,

treated in my apparatus with hydriodic acid, did not give any iodide of silver.

The presence of small quantities of carbonate of sodium in the lye is perfectly negligible. We have therefore only to reckon with the sulphur compounds, which are easily removed, and in more exact analyses with those of chlorine, which are also easily got rid of.

I think it is as well to give the results of some estimations of glycerin made; the first after eliminating the sulphuric acid, the second after eliminating both the chlorine and the sulphuric acid.

100 c.c. of soap-lye were diluted with an equal volume of water, precipitated hot with acetate of baryta to eliminate the sulphuric acid, and, after cooling, the liquid was made up to 500 c.c. with water. Five c.c. of the filtered liquid, corresponding to 1 c.c. of the soap-lye, were treated in the hydriodic acid apparatus. The duration of each operation was two hours. The results obtained were:—

I. 0.2102 gram. AgI, representing 8.25 per cent of glycerin.

II. 0.2007 gram. AgI, representing 7.87 per cent of glycerin.

In none of the duplicate estimations made by me up to the present has the difference between the results been so marked. Such a difference denotes the presence of substances which interfere with the reaction, chloride of sodium in the present case.

In the second experiment, 20 c.c. of the lye diluted with 80 c.c. of water, were treated with a quantity of solid sulphate of silver corresponding to the proportion of chloride of sodium in the lye. By heating on the water-bath the formation of the precipitate of chloride of silver is complete in a few minutes. After removing the sulphuric acid by means of acetate of baryta, we filter, wash the precipitate, and evaporate the filtrate and the wash-waters combined, down to 70 c.c., and after cooling add to the liquid enough water to bring it up to 100 c.c. Five c.c. of this solution, representing 1 c.c. of the soap-lye, gave the following results:—

I. 0.2125 gram. AgI, representing 8.34 per cent of glycerin.

II. 0.2129 gram. AgI, representing 8.35 per cent of glycerin.

Relying on the results of these experiments I propose the following method for the estimation of glycerin in residuary soap-lyes:—

Putting on one side a possible error of a few tenths per cent, we treat 20 c.c. of the lye with once or twice its volume of water, precipitate hot with acetate of baryta to eliminate the sulphuric acid, filter, and make up the volume to 100 c.c., then treat 5 c.c. of this solution with hydriodic acid in the apparatus already described. On the other hand, if we wish to obtain very exact results, we dilute 20 c.c. of the lye with two or three times its volume of water, treat the liquid with solid sulphate of silver in quantity necessary to precipitate the chlorine in the form of chloride of silver, heat on the water-bath, and precipitate the sulphuric acid with acetate of baryta. After having filtered and washed the precipitate, we evaporate the filtrate and the wash-waters down to 80 c.c. After cooling, make up the volume to 100 c.c., and estimate the glycerin on 5 c.c. of this liquid.—*Zeitschrift für Angewandte Chemie*, 1903, p. 413.

The Geological Society of London will this year award its Medals and Funds as follows:—The Wollaston Medal to Dr. J. J. Harris Teall, M.A., F.R.S.; the Murchison Medal to Mr. Edward John Dunn, of Melbourne; the Lyell Medal to Dr. Hans Reusch, Director of the Geological Survey of Norway; the Bigsby Medal to Prof. J. W. Gregory, D.Sc., F.R.S. The Wollaston Fund to Mr. H. H. Arnold-Bemrose, M.A.; the Murchison Fund to Mr. H. L. Bowman, M.A.; the Lyell Fund to Mr. E. A. Newell Arber, M.A., and Mr. Walcott Gibson.

SOLUBILITY OF GOLD IN CERTAIN OXIDISING AGENTS.*

By VICTOR LENHER.

THE inactive character of gold is so pronounced that towards many of the reagents the element is quite indifferent; in fact, almost the only solvents in general use for dissolving the metal are chlorine, bromine, or a solution of alkaline cyanide in presence of atmospheric oxygen. Chlorine and bromine attack the metal readily, while iodine only dissolves the metal when it is freshly liberated, or under other very favourable circumstances. The metallic perchlorides, perbromides, and periodides, according to Nicklès, dissolve gold, the lower halides of the metal being formed along with gold chloride (*Ann. Chim. Phys.*, [4], x., 318). Hot selenic acid readily dissolves gold. Iodic acid has slight action on the metal, while, according to Prat, a mixture of iodic and sulphuric acids dissolves gold when heated to 300° (*Comptes Rendus*, lxx., 840). This reaction has been verified by the author, who also finds that gold is readily soluble in a mixture of hot sulphuric and periodic acids.

Gold is also slightly soluble in the alkaline sulphides and thiosulphates (Studefelt, "Lixiviation of Silver Ores," pp. 15, 38).

There is another class of substances, substances which evolve oxygen when treated with acids, whose action on gold has received very little attention.

Several years ago the author had occasion to review the work of Mitscherlich on the solubility of gold in selenic acid, and showed that gold is readily attacked by pure hot selenic acid with the formation of auric selenate.

In following the same line of work with telluric acid, which in many respects is closely analogous to selenic acid, the obstacle is met that telluric acid is a solid. This apparent difficulty can be obviated by first dissolving the crystalline telluric acid in sulphuric or phosphoric acid. Such a solution of telluric acid, when heated, dissolves metallic gold.

With the fact at hand that at the same temperature at which selenic acid or a solution of telluric acid attacks gold, the acids themselves are broken down into the dioxides and oxygen, it appeared probable that the solvent action in these cases was due to the production of oxygen in the reaction. Should this view be correct, gold should be soluble in acids when an oxidising agent is present. The action of a large number of substances, such as oxides of various types, sulphates, &c., was tried on gold in presence of sulphuric, phosphoric, and arsenic acids, and only such substances as give oxygen in presence of the acids will act on gold. In most cases, the only precautions necessary in order to demonstrate the solvent action is to have the acids in a high degree of concentration.

All of the substances that have been used in the following experiments were carefully tested for the halogens, and only such substances used as were halogen-free. In many instances the substances had to be prepared in order to obtain them in a high degree of purity. The author wishes to acknowledge the services of Mr. Geo. Kemmerer, who greatly assisted the work at many points, both in preparing many of the substances used and in confirming the reactions.

The first substance that was naturally examined was manganese dioxide, as it is well known that manganese dioxide gives oxygen when heated with sulphuric acid. A mixture of manganese dioxide and sulphuric acid, when heated for a few minutes with gold, causes the metal to go into solution. On diluting the solution and testing with oxalic acid or ferrous sulphate, all of the gold is precipitated. In working with manganese dioxide and sulphuric acid, practically the only precaution necessary is to have the acid concentrated. Solution of gold in presence of manganese dioxide and sulphuric acid takes place readily when the mixture is hot, but the reaction also

takes place in the cold. A mixture of manganese dioxide and sulphuric acid, when allowed to remain in contact with gold leaf for twelve hours at 0°, will dissolve sufficient gold to give an appreciable precipitation, when the mixture is diluted and treated with ferrous sulphate. It is thus seen that while heat accelerates the reaction, solution nevertheless takes place at low temperatures.

The higher oxides of manganese act in an entirely similar manner. The substances actually worked with were manganese dioxide (a) native, (b) from the ignition of manganese nitrate, (c) by the action of bromine on manganese acetate:—Manganese sesquioxide (Mn_2O_3), manganese protosulphate (Mn_3O_4), and potassium permanganate. The solvent action takes place in a similar manner when phosphoric or arsenic acid is substituted for sulphuric, but the action is greatly moderated.

In 1872 Allen (*CHEMICAL NEWS*, xxv., 85) showed that when solid potassium permanganate and sulphuric acid are heated for a few minutes with precipitated gold the solution becomes nearly clear, and on diluting and testing with oxalic acid or ferrous sulphate the solution was found to contain abundance of gold.

This experiment has been repeated, using sulphuric acid as described by Allen, and also by substituting phosphoric for the sulphuric acid. In all cases solution takes place and the gold can be readily detected by ferrous sulphate.

Lead dioxide, lead sesquioxide, and red lead, when used with sulphuric acid, cause gold to enter into solution. The action takes place more readily in the warm than in the cold, though at the ordinary temperatures solution does actually take place, gold being found in the solution after several hours' contact.

With the higher oxides of lead, phosphoric acid can be substituted for the sulphuric acid, solution being effected. With chromium trioxide, chromium tetroxide, and nickel oxide, solution of gold is effected in presence of sulphuric or phosphoric acids, the reaction taking place, though moderated, in the cold.

When nitric acid is subjected to heat, more or less decomposition is effected, part of the acid breaking down into nitrogen dioxide and oxygen. This reaction can be used in a highly satisfactory manner to demonstrate the solubility of gold in sulphuric acid in presence of an oxidising agent. This reaction was first noted by Reynolds (*CHEMICAL NEWS*, x., 48, 167, 277), and later by Spiller (*CHEMICAL NEWS*, x., 173). The results which these chemists obtained have been confirmed by the author, and show that when a mixture of hot nitric and sulphuric acids comes in contact with gold the metal enters into solution and, at the same time, a lower oxide of nitrogen is formed by the reduction of the nitric acid, and this oxide remains in the solution.

That a lower oxide of nitrogen is present in the solution after the gold has dissolved can be demonstrated in a very pretty manner, as Spiller has shown, by adding the solution to water when the metal is thrown out as a purple precipitate. Allen (*CHEMICAL NEWS*, xxv., 85) later showed that this precipitation by water from nitric-sulphuric acid solution is due to the presence of a lower oxide of nitrogen, probably nitrous acid, since when the water used for dilution contains potassium permanganate no precipitation takes place. Also ammonium sulphate destroys the nitrous acid, and, after boiling with ammonium sulphate, no precipitation takes place, while when fuming nitric acid is added to any of the liquids, the gold is thrown down, purple in colour. While Reynolds, Spiller, and Allen have studied the reaction of a mixture of hot nitric and sulphuric acids on gold, the influence of temperature on the reactions seems to have escaped their attention, and also that certain other acids, as phosphoric acid, can be substituted for the sulphuric acid with practically as great solvent action taking place.

While a mixture of nitric acid with either sulphuric acid or phosphoric acid readily acts on gold when warm, solution actually takes place, though more slowly, even at zero.

* Read at the St. Louis Meeting of the American Chemical Society. From the *Journal of the American Chemical Society*, xxvi., No. 5.

The action of oxygen gas on gold leaf, suspended in hot sulphuric acid, was also tried, but neither oxygen nor ozone would cause any of the metal to pass into solution.

The anode oxygen, obtained in electrolysis, was next studied as to its action on gold. Bunsen noticed, when using for the electro-decomposition of water an apparatus in which the platinum electrodes were connected with the terminals by means of gold solder, that on electrolysis in presence of dilute sulphuric acid there is a film of oxide formed on the gold. Later it was shown by Spiller that when a plate of metallic gold is made the anode and a piece of platinum foil or gauze used as the cathode in an electrolyte of sulphuric acid or a mixture of nitric and sulphuric acids, the gold anode dissolves and the metal was deposited on the cathode, the source of the current used being a few Grove cells.

This work, which has been repeatedly verified, demonstrates that in presence of strong sulphuric acid, solution of gold can be effected readily by means of anode oxygen, the action proceeding rapidly when the acid is hot. On the other hand, when the acid is dilute the oxide of gold formed does not pass through the solution and deposit on the cathode as metal, but remains as an incrustation on the gold anode. Here again a similar series of results is obtained when phosphoric acid replaces the sulphuric. When solutions of the acid sulphates of potassium or sodium are used as electrolytes, the action goes on exactly as above indicated. If the solution contains sufficient free acid, gold passes through the electrolyte, while if the solution is dilute or contains only a little free acid, the oxide remains as a film on the anode.

In the case of an alkaline electrolyte, such as a solution of sodium or potassium hydroxide, it is possible for some of the gold to pass through the solution, probably from the formation of aurate of the alkali. Such is actually the case, although in alkaline solution a large amount of oxide remains as an incrustation on the gold anode employed. When neutral salt solutions are employed as electrolytes, such as the nitrates or sulphates of potassium or sodium, very little, if any, of the gold can pass through the electrolyte, and as a result the anode is converted into the oxide Au_2O_3 . Here we have the last step in the series of experiments, viz., obtaining the gold oxide in pure condition and retaining it as such.

In the above series of experiments the current used was 0.3 to 0.5 ampere at a pressure of 5 volts, the anode being a sheet of gold and the cathode a 20-grm. platinum crucible. In such experiments where gold was deposited on the crucible, the quickest method found for removing the metallic deposit, which frequently appeared as a hard plating, was found to be the hot mixture of nitric and sulphuric acids, as indicated above. This method was found to be vastly superior to that of the use of a cyanide solution, such as was at first used.

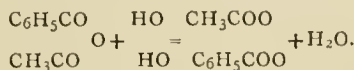
It thus appears that gold is not only attacked by the halogens, but is also readily attacked in a large number of reactions in which oxygen is produced, these latter reactions taking place readily in the warm solutions, but slowly even at as low a temperature as zero. Furthermore, it appears that it is necessary for the oxygen to be produced in the mixture, and that ordinary oxygen gas, when conducted into sulphuric acid in which gold leaf is suspended, will not cause the gold to dissolve.

The Royal Sanitary Institute.—The Saxon Snell Prize was founded to encourage Improvements in the Construction or Adaptation of Sanitary Appliances, and to be awarded by the Council of the Royal Sanitary Institute at intervals of three years, the funds being provided by a legacy bequeathed to the Institute for this purpose by the late Henry Saxon Snell, F.R.I.B.A. The first prize, which will consist of £50 and a medal of the Institute, is offered in the year 1905 for an essay on "Domestic Sanitary Appliances, with Suggestions for their Improvement."

THE ACTION OF HYDROGEN PEROXIDE UPON ANHYDRIDES, AND THE FORMATION OF ORGANIC ACID, PEROXIDES, AND PERACIDS.*

By A. M. CLOVER and A. C. HOUGHTON.

NEF has shown that pure hydrogen peroxide and acetic anhydride reacting with each other yield acetic peroxide (*Liebig's Ann. Chem.*, ccxcviii., 287). Baeyer found that the same substance was formed by the action of acetic anhydride upon an aqueous solution of hydrogen peroxide (*Ber.*, xxxiii., 1569). Neither of these authors attempt to explain the reaction which takes place, and one might be led to suppose that the peroxide was formed by the direct addition of oxygen to the anhydride. In considering the reaction of hydrogen peroxide upon benzoyl acetyl oxide, however, Nef assumes the following reaction to take place:—



In attempting to prepare other peroxides by the action of anhydrides upon hydrogen peroxide we have found that only the anhydrides of the simple acids react with hydrogen peroxide, i.e., anhydrides which are acted upon by water. Even when the more complex and less soluble anhydrides are brought together with hydrogen peroxide in ethereal solution, there is no reaction.

From experimental facts, which will be brought out later in this article, it will be seen that the action of hydrogen peroxide upon anhydrides is not a simple one; that the reaction is very similar to that of water upon anhydrides, and the formation of peroxides depends upon two distinct reactions.

Changes in Acetic Peroxide when Dissolved in an Aqueous Solution of Hydrogen Peroxide.

The changes which an aqueous solution of acetic peroxide undergoes have been previously studied by one of the authors in connection with G. F. Richmond (*Am. Chem. Journ.*, xxix., 179). It was found that the substance was hydrolysed with the formation of acetic acid and acetic peracid, and it was shown that acetic peracid could be distinguished from acetic peroxide by its very rapid action upon potassium iodide. The action of acetic peroxide in dilute solution upon potassium iodide, if the latter be not in large excess, is so slow that the iodine liberated by the peracid may be estimated with little error.

We have found that when acetic peroxide is dissolved in a solution of hydrogen peroxide there is a similar change into peracid, but that the amount of peracid in the solution is more than can be accounted for by the reaction of the peroxide upon water; moreover, that there is a gradual loss of hydrogen peroxide in the solution, the active oxygen of which is found combined with the acetyl group. In order to follow these changes, it is necessary to be able to accurately estimate hydrogen peroxide, acetic peroxide, and acetic peracid in the presence of each other.

In dilute solutions containing no mineral acid, the action of hydrogen peroxide, as well as acetic peroxide, upon potassium iodide, is so slow that with practice one may accurately estimate peracid by adding a drop or two of strong potassium iodide solution, and titrating immediately with thiosulphate. If only a small amount of potassium iodide is added, there need be no especial hurry in making the titration; after the removal of the "immediate" iodine, the further liberation can be seen to be very slow. It too much potassium iodide is used it is necessary to operate quickly, and to make a preliminary titration to obtain approximately the amount of thiosulphate required; the estimation may then be made quickly.

* From the *American Chemical Journal*, xxxii., No. 1.

In either case, after a little practice, one may satisfy himself of the accuracy of the result.

The estimation of hydrogen peroxide may be accurately made by adding to a large excess of dilute sulphuric acid (2N acid was used), and titrating with permanganate. It has been previously shown that peracids oxidise manganous salt to permanganic acid, and that this action interferes with the estimation as ordinarily made; however, in very dilute solution, which is strongly acidified, this action is so retarded that there is little error.

The following experiments illustrate the accuracy of the method:—

Ten c.c. of a solution of commercial hydrogen peroxide titrated with N/20 permanganate in the ordinary manner required 23.7 c.c. A strong solution of pure acetic peroxide* was made, and allowed to stand for four hours. At the end of this time the peracid in 1 c.c. of the solution was represented by 6.1 c.c. N/20 thiosulphate; the unchanged peroxide by 6.6 c.c. Only a trace of hydrogen peroxide had been developed.

Separate portions, of 10 c.c. each, of the above solution of hydrogen peroxide were then each diluted to 300 c.c. with dilute sulphuric acid, and cooled to 10°. To the first was then added 1 c.c. of the above solution of acetic peroxide and peracid, to the second 2 c.c., to the third 3 c.c., and to the fourth 4 c.c. These solutions were then titrated with N/20 permanganate.

	Required. C.c.
1.	23.65
2.	23.60
3.	23.65
4.	23.55

In the fourth solution the amount of active oxygen as peracid was nearly equal to that as hydrogen peroxide. To obtain accurate results it is necessary to make the titration quickly, and to do this it is necessary, in case the amount of hydrogen peroxide in the solution is unknown, to make a preliminary titration in order to obtain approximately the volume of permanganate required.

The acetic peroxide cannot be directly estimated, but may be obtained by difference after estimating the total active oxygen. This may be accurately done by dissolving in a small amount of 20 per cent acetic acid containing potassium iodide, and allowing to stand for half-an-hour, then diluting and titrating with thiosulphate. Careful experiments with known quantities of hydrogen peroxide, acetic peroxide, and acetic peracid have shown that all of these substances may be accurately estimated in this way. A correction obtained from a blank solution may be applied.

A solution of commercial hydrogen peroxide containing 30.5 grms. per litre was nearly saturated with pure acetic peroxide. The contents of the solution were estimated as quickly as possible after it was made, and then at intervals. The temperature of the solution remained constant, 23°.

For the estimation of hydrogen peroxide 1 c.c. of the solution was removed, and diluted to 100 c.c. Fifty c.c. of this were removed, and after diluting to 300 c.c. with dilute sulphuric acid, were titrated with N/20 permanganate, as already described. This number multiplied by 2 is the one given in the table.

For the estimation of peracid, 1 c.c. of the solution was added to 300 c.c. of water, a small amount of potassium iodide solution added, and the iodine liberated was titrated quickly with N/20 thiosulphate.

The total active oxygen contained in 1 c.c. of the solution was determined by dissolving in 6 or 7 c.c. of a 20 per cent solution of acetic acid containing potassium iodide, and allowing to stand for one-half hour. The solution was then diluted, and the free iodine estimated with N/20 thiosulphate. Only a slight correction, amounting to about 2 drops of thiosulphate, is necessary.

* The acetic peroxide used in this work was prepared according to the method of Clover and Richmond (*loc. cit.*), and was re-crystallised from ligroin just before using.

The three portions to be estimated were removed from the original solution as quickly as possible after each other. After being diluted as described no further change takes place in the diluted solution during the time necessary to carry on the estimations.

Time in hours.	N/20 thio-sulphate (immediate).	N/20 thio-sulphate total.	N/20 permanganate.	N/20 thiosulphate representing acetic peroxide.
	C.c.	C.c.	C.c.	C.c.
—	—	48.5	35.0	13.5
2	6.7	48.0	31.7	9.6
7	12.7	47.5	28.8	6.0
24	13.9	46.1	27.8	4.4

An inspection of these figures brings out the following facts:—

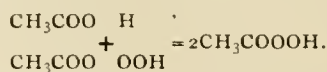
1. At the end of two hours the amount of active oxygen as peracid in the solution is just one-half of that originally present as peroxide. The formation of peracid is therefore much faster than in aqueous solution (Clover and Richmond, *loc. cit.*).

2. The amount of hydrogen peroxide in the solution rapidly decreases; further, the solution gradually loses in total active oxygen, but the loss in hydrogen peroxide is much greater than the loss in total active oxygen.

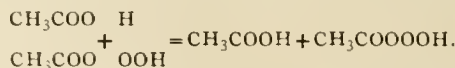
3. At each interval the total active oxygen present as peroxide and peracid is considerably greater than that originally present as peroxide. Acetic peracid is therefore formed at the expense of the active oxygen of the hydrogen peroxide.

The solution of hydrogen peroxide employed contained a small amount of soluble mineral matter, which has a much greater catalytic action upon acetic peracid than upon hydrogen peroxide. This partly accounts for the loss in active oxygen; however, this loss was greatest during the first stages of the reaction at the time when the amount of peracid was smallest. Active evolution of oxygen in the solution was most noticeable during the first hour or two. The greater part of the loss is therefore intimately connected with the reaction itself. During the last stages of the reaction the peracid is evidently decomposed faster than it is formed.

The action of hydrogen peroxide upon acetic peroxide resulting in the formation of more peracid than would be formed by the ordinary hydrolysis, is most easily explained as follows:—



Owing to the instability of the substances in question it is not possible to say that they react in the proportion indicated. The reaction suggests that of water upon acetic peroxide. Looked on in this light the possibility of a reaction, according to the following equation, suggests itself:—



Assuming such a reaction to take place, the loss of oxygen, already referred to, would be accounted for by the instability of the substance CH_3COOOOH , a derivative of the hypothetical trioxide of hydrogen.

A number of experiments, similar to the one described, were carried out with different solutions of hydrogen peroxide, and in all cases the same general results were obtained.

Action of an Aqueous Solution of Hydrogen Peroxide upon Acetic Anhydride.

When acetic anhydride is dissolved in hydrogen peroxide solution both acetic peracid and peroxide are soon present in the solution. The peracid in the solution may result

from the hydrolysis of previously formed peroxide, or it may be formed directly by the action of hydrogen peroxide upon anhydride. A study of the rates of formation of these two substances has led to the conclusion that the peracid is the first substance formed.

The rate of formation of peracid in solutions of hydrogen peroxide of different strength is shown in the table given below. The best commercial hydrogen peroxide was used, which was concentrated to the strength given by distillation in a vacuum. The acetic anhydride was fractionated before using.

Twenty c.c. of hydrogen peroxide solution (61.6 grms. per litre) were brought to a temperature of 21°, and 1 c.c. of acetic anhydride added. The latter was dissolved quickly by shaking, and the solution was kept at 21°. At different intervals, 1 c.c. of the resulting solution was removed, and the peracid present estimated in the manner already described. As the intervals of time are necessarily small, on account of the rapidity of the reaction, it was necessary to fill the pipette just before the time indicated, and at the proper time to deliver the solution into a large volume of water, in order to stop or greatly retard any further reaction between the constituents. The results obtained appear in the first column below. In the second column are the results of a duplicate experiment carried out in exactly the same manner.

A solution of hydrogen peroxide of different strength (45.4 grms. per litre) was also employed. The experiments with this solution were carried out in exactly the same way as described above, all conditions and measurements being the same. The results duplicated are placed in columns III. and IV.

Time in minutes.	I. N/20 thiosulphate.	II. N/20 thiosulphate.	III. N/20 thiosulphate.	IV. N/20 thiosulphate.
3	1.0	1.0	0.7	0.75
6	1.4	1.3	0.9	0.9
9	1.6	1.5	1.0	1.0
12	1.7	1.65	1.1	1.1
15	1.8	1.75	1.2	1.2
18	1.9	1.95		
21		2.2		
27		2.5		
30		2.6		

It will be noted that the rate of formation of peracid is large at first, but is soon checked. So long as acetic anhydride is present in the solution there would be a limit to the concentration of peracid owing to the ready reaction between the two substances (Clover and Richmond, *loc. cit.*).

As soon as anhydride is removed from the solution, the formation of peracid by the hydrolysis of peroxide should continue at a uniform rate. To determine whether or not the relatively large amounts of peracid present in the solution at the earlier intervals can be accounted for by the hydrolysis of peroxide present, necessitates a determination of the amount of the latter substance in the solution at different intervals.

The amount of acetic peroxide was obtained as in the previous case, by subtracting from the total active oxygen the sum of the active oxygen as hydrogen peroxide and as peracid. The total active oxygen was obtained in the manner already described. The hydrogen peroxide was also estimated as previously described. Careful experiments showed that a known amount of hydrogen peroxide could be accurately estimated under the conditions employed, and in the presence of the maximum amount of peracid, peroxide, and anhydride which might be in the solution to be examined. As this determination is of vital consequence to the results obtained and the conclusions drawn, a few of these experiments will be given.

A definite volume of hydrogen peroxide solution was estimated in the usual manner with N 20 permanganate. Required, 16.8 c.c.; duplicated, 16.85 c.c.

(To be continued).

NOTICES OF BOOKS

Work and Wages. Part I. Foreign Competition. By SYDNEY J. CHAPMAN, M.A. London, New York, and Bombay: Longmans, Green, and Co. 1904.

THIS book may be regarded as a sequel to Lord Brassey's "Work and Wages," published in 1872, and to the same author's later book on "Foreign Work and English Wages," published in 1879, and contains an introduction by Lord Brassey, in which a brief summary of the subject-matter is given, with a few valuable generalisations of the lessons to be learnt from the results of the author's investigations. Prof. Chapman has succeeded in very judiciously weighing the evidence he has collected, and in giving a fair and unbiased statement of the condition of affairs in many of the most important industries, compiled from the best authorities. The chapter on chemicals and dyes, which are considered with special reference to advances made by German manufacturers, contain many references to Mr. Evershed's paper on "Statistics of Chemical Imports and Exports of the United Kingdom and Germany in the Year 1901," which appeared in the *Journal of the Society of Chemical Industry*, April, 1903, and the case of the aniline dyes is investigated in some detail. The work, which is written in a style which is necessarily somewhat dogmatic without being controversial, is most interesting, and is well worth careful study both by manufacturers and by students of economics. The author takes a by no means pessimistic view either of British work or British workmen, but, on the other hand, he shows no inclination to shirk obvious facts, however unpalatable may be the lesson they seem to teach.

Smoke Prevention and Fuel Economy. By WM. H. BOOTH, M.Amer.Soc.C.E., and JOHN B. C. KERSHAW, F.I.C. London: Archibald Constable and Co., Ltd. 1904.

THIS book cannot lay claim to any special novelty in treatment or in the suggestions put forward for the abatement of the smoke nuisance, which the authors ascribe chiefly to the adoption of American steam practice in this country. The book is based upon the work on "Rauchplage und Brennstoffverschwendung" of Ernst Schmatolla, which the authors at first intended to translate in full; finding, however, that to fit the book for the use of English engineers many fundamental alterations would have to be made on account of the great differences existing between German and English practice, they decided to produce an original work, taking the German work more or less as a model. In order to keep before the practical man's mind a due sense of the importance of a thorough knowledge of the scientific principles of combustion, a chapter of considerable length is devoted to the chemistry of the process. This chapter is marred by a certain vagueness and looseness of expression, specially noticeable in the discussion of the occurrence of hydrogen in coal, which at first sight certainly conveys a wrong impression. The examination of the waste gases is also treated, not, however, quite as fully as the magnitude and importance of the subject might be supposed to demand. The chapters on the Improved Methods of Burning Fuels contain no very striking suggestions, and the domestic smoke problem is altogether excluded from the book, which, however, gives an acceptable summary of the more general methods which have been employed or proposed for the purposes in question.

Grundzüge der Chemischen Pflanzenuntersuchung ("The Outlines of the Chemical Examination of Plants"). By Dr. L. ROSENTHALER. Berlin: Julius Springer. 1904.

THIS small book gives in a handy form a description of the methods of extraction of substances mostly of medicinal, technical, or scientific importance, from the plant structure,

and the only fault to find with it is that the treatment is somewhat too curtailed. Thus while the practical extraction and purification of various alkaloids, glucosides, fats, oils, carbohydrates, and inorganic constituents is explained, we find in the book no references to the constitution or nature of these classes of compounds, or to the relations of the various compounds to one another, and the treatment of practical details is also somewhat meagre, as, for instance, in the description of the methods of fractional precipitation. However, regarded as merely a collection of notes, the book, which covers ground which has been somewhat neglected, both by chemists on the one hand, and botanists on the other, will no doubt find a circle of readers to appreciate its many good points and to overlook its comparatively few defects.

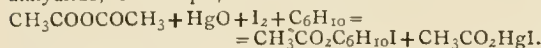
CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxix., No. 24, December 12, 1904.

The Element Z_{41} .—M. Lecoq de Boisbaudran.—The author discusses M. Urbain's paper in the *Comptes Rendus* of November 7 on the subject of the element Z_{41} . He believes that unless the band 487.7 depends on an element previously known and thoroughly well identified before the announcement of Z_{41} , the discovery of Z_{41} is his own work.

New Addition Derivatives of Tetrahydrobenzene.—Léon Brunel.—The action of iodine and mercury oxide on cyclohexene in presence of various reagents give rise to etheral derivatives of hydro-aromatic glycols. By effecting the same reaction with anhydrides of the organic acids the author obtains new ethers of the same glycols. These reactions are similar to those already described, 2 mols. of cyclohexene react on 1 mol. of mercury oxide, and 4 atoms of iodine in presence of 1 mol. of anhydride. These reactions take place in two phases. In the case of acetic anhydride, for example, the action is:—



There is thus formed an acetoiodide of mercury with a first molecule of acetic ether and glycol iodide. During the second phase of the reaction two other atoms of iodine react on the mercury acetoiodide and the cyclohexene, $\text{CH}_3\text{CO}_2\text{HgI} + \text{I}_2 + \text{C}_6\text{H}_{10} = \text{CH}_3\text{CO}_2\text{C}_6\text{H}_{10}\text{I} + \text{HgI}_2$, giving a second molecule of acetine iodohydrine, whilst all the mercury passes into the state of biniodide.

Synthesis and Investigation of Substituted Cyclic Thio-hydantoinines.—Emm. Pozzi-Escot.—The di-substituted cyclic thiourated products, of which the author gives a general method of preparation in a previous paper, lead to the preparation of certain di-substituted symmetric *a-b*-ethyloyl-thiourides, which were not previously known. The method of preparation consists in acting on the *a-b*-disubstituted thiourated bodies with a mono-halogen ethanoic acid, either mono-chloroacetic acid or mono-bromoacetic acid. Di-substituted sulpho-hydantoin is formed with excellent yield, often more than 90 per cent of the theoretical yield.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxxi., No. 5.

The Dissociation of the Alkaline Carbonates.—P. Lebeau.—Already noticed.

General Relations between the Heat of Combustion of Organic Compounds and their Constitution. Calculation of the Heats of Combustion.—L. Leniout.—Already noticed.

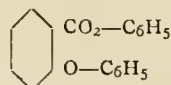
Aluminium Powder and the Oxidation of Aluminium.—E. Kohn-Abrest.—Already inserted in full.

Influence of the Physical Nature of the Anode on the Constitution of Electrolytic Peroxide of Lead. Application to Analysis.—A. Hollard.—Already inserted in full.

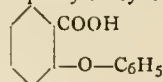
Formation of Symmetrical Diphenylised Pyrones by the Action of Alkaline Carbonates on the Orthophenylphosphoric Ethers.—R. Fosse.—As a rule the orthophenylphosphoric ethers, in the presence of various salts, give reactions of double composition. Orthophosphate of phenyl and cyanide of potassium are transformed into potassic phosphate and benzoic nitrile, $\text{PO}_4(\text{C}_6\text{H}_5)_3 + 3\text{KCN} = \text{PO}_4\text{K}_3 + 3\text{C}_6\text{H}_5\text{CN}$. By analogy, phosphate of phenyl and carbonate of potassium ought to give potassic phosphate and carbonate of phenyl, $2\text{PO}_4(\text{C}_6\text{H}_5)_3 + 3\text{CO}_2\text{K}_2 = 2\text{PO}_4\text{K}_3 + 3\text{CO}_2(\text{C}_6\text{H}_5)_2$. However, on distilling a mixture of the two substances no diphenylcarbonic ether is formed, but torrents of carbonic anhydride, phenyl, and diphenopyrone, or xanthone, are given off, $\text{C}_6\text{H}_4 < \overset{\text{CO}}{\text{O}} > \text{C}_6\text{H}_4$, and a small quantity of oxide

of phenyl. By submitting several phosphates of the phenols to this reaction, we are able to obtain the corresponding diphenylised pyrones. By the action of carbonate of potassium on orthophosphate of phenyl, an abundant evolution of carbonic anhydride is observed, and on distillation a complex oil is obtained, which becomes partially solidified into fine yellow crystals; on fractionating this substance we obtain:—1. Phenol. 2. A small quantity of oxide of phenyl, characterised by its odour, its boiling-point 250—255°, and its insolubility in soda. 3. An amber coloured liquid, passing over at 350—360°, becoming rapidly solidified into a crystalline mass, slightly yellow in colour. The author also describes the action of carbonate of potassium on orthophosphate of orthocresol, which gives dimethyldiphenopyrone, and of carbonate of potassium on the phosphate of α -naphthol, producing α -dinaphthopyrone.

Transformation of the Diphenylcarbonic Ether into Orthophenoxybenzoic Acid, and into Orthophenoxybenzoate of Phenyl.—R. Fosse.—If we heat this ether, $\text{CO}_2(\text{C}_6\text{H}_5)_2$, in the presence of neutral carbonate of potassium or sodium, we observe large bubbles of gas form on the deposit of the alkaline salt, and disappear at the surface of the liquid. With very little carbonate of sodium, the carbonate of phenyl decomposes into CO_2 , phenol, orthophenoxybenzoate of phenyl, or diphenylsalicylic ether,—



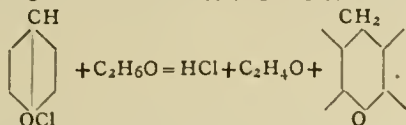
a trace of oxide of phenyl, $(\text{C}_6\text{H}_5)_2\text{O}$, and orthophenoxybenzoic acid, or monophenylsalicylic ether,—



With a large excess of an alkaline carbonate we obtain CO_2 , phenol, principally of phenoxybenzoic acid, $\text{C}_6\text{H}_4 < \overset{\text{CO}_2\text{H}}{\text{O}} - \text{C}_6\text{H}_5$, a trace of oxide of phenyl and a small quantity of phenoxybenzoate of phenyl, $\text{C}_6\text{H}_4 < \overset{\text{CO}_2 - \text{C}_6\text{H}_5}{\text{O}} - \text{C}_6\text{H}_5$. Thus, with a small or a large amount of carbonate of soda, we can obtain, besides the CO_2 and the phenol, almost exclusively either the phenoxybenzoate or phenoxybenzoic acid.

Transformation of Phenols into Symmetrical Diphenylised Pyrones, and of Pyrones into Pyranes.—R. Fosse and A. Robyn.—These experiments were carried out on paracresol thymol. The two phenols, treated with oxychloride of phosphorus, gave the two corresponding orthophosphates. These latter, distilled in the presence of neutral carbonate of potassium, produced carbonic acid

gas, pyrone, and phenol, corresponding to the phosphate. By the intermediary of the orthophosphate the authors passed from the paracresol to the dimethylidiphenolpyrone, and from thymol to dimethylidipropylidiphenolpyrone. The pyrones were transformed into pyranols by the fixation of 1 molecule of hydrogen. The pyranols, treated with hydrochloric acid, gave salts of pyryl. The salts of pyryl, in the presence of alcohol, gave the curious oxidising reaction already described by one of us; the alcohol is oxidised to aldehyde, one of the two atoms of hydrogen resulting from this transformation goes to the chlorine of the salt of pyryl, giving HCl, while the second atom of hydrogen goes to the radical pyryl giving pyrane,—



Two New Orthophenoxybenzoic Acids.—R. Fosse and A. Robyn.—The two new acids described in this paper were prepared by treating the carbonates of para- and ortho-cresol with carbonate of sodium. When heated with sulphuric acid they are converted into pyrones. They are the paracresyloxy-*p*-cresylorthomethyloic acid, and the orthocresyl-oxy-orthocresylorthomethyloic acid.

Nitric Ethers of the Acid Alcohols.—H. Duval.—Already noticed.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, January 17, at 5 o'clock, Prof. L. C. Miall begins a course of six lectures on "The Structure and Life of Animals"; on Thursday, January 19, at the same hour, Prof. Churton Collins delivers the first of two lectures on (1) "The Religion of Shakespeare," (2) "The Philosophy and Significance of 'The Tempest'"; and on Saturday, January 21, at 3 o'clock, Prof. Oman commences a course of two lectures on "Wat Tyler in London." The Evening Discourse on Friday, January 20, will be delivered by Prof. Sir James Dewar on "New Low Temperature Phenomena," and on January 27 by Dr. E. A. Wilson, Assistant Surgeon to the National Antarctic Expedition, on "The Life History of the Emperor Penguin."

The Iron and Steel Institute.—*The Andrew Carnegie Research Scholarship.*—A Research Scholarship or Scholarships, of such value as may appear expedient to the Council of the Iron and Steel Institute from time to time, founded by Mr. Andrew Carnegie (President), who has presented to the Iron and Steel Institute sixty-four one-thousand dollar Pittsburg, Bessemer, and Lake Erie Railroad Company Five per cent Debenture Bonds for the purpose, will be awarded annually, irrespective of sex or nationality, on the recommendation of the Council of the Institute. Candidates, who must be under thirty-five years of age, must apply on a special form before the end of February to the Secretary of the Institute. The object of this scheme of scholarships is not to facilitate ordinary collegiate studies, but to enable students, who have passed through a college curriculum or have been trained in industrial establishments, to conduct researches in the metallurgy of iron and steel and allied subjects, with the view of aiding its advance or its application to industry. There is no restriction as to the place of research which may be selected, whether university, technical school, or works, provided it be properly equipped for the prosecution of metallurgical investigations. The appointment to a scholarship shall be for one year, but the Council may at their discretion renew the scholarship for a further period instead of proceeding to a new election. The results of the research shall be communicated to the Iron and Steel Institute in the form of a paper to be submitted to the Annual General Meeting of members, and if the Council consider the paper to be of sufficient merit, the

Andrew Carnegie Gold Medal shall be awarded to its author. Should the paper in any year not be of sufficient merit, the Medal will not be awarded in that year.—By Order of the Council, BENNETT H. BROUGH, Secretary.

Sulphocyanide of Copper.—Hermann Grossmann.—The author has attempted to prepare double compounds corresponding to the copper salt, $\text{CuCN} \cdot 2\text{KCN} \cdot \text{CuCNS} \cdot 4\text{H}_2\text{O}$, easily obtained by dissolving sulphocyanide of copper in cyanide of potassium (we take 1 molecule of commercial cyanide of copper + 2 molecules of $\text{KC}_y + 1$ molecule of sulphocyanide of potassium). With sulphocyanide of ammonium, under analogous conditions, we obtain $2\text{CuCNS} \cdot 3\text{NH}_4\text{CNS}$. By dissolving cyanide of copper in very concentrated solutions of an alkaline sulphocyanide (such as potassium or ammonium), we obtain the double salts $2\text{CuCN} \cdot 3\text{CNSM}$, which crystallise in rhombic plates.—*Zeit. Anorg. Chem.*, vol. xxxvii., p. 407.

Distillation in vacuo in Quartz Vessels.—Alois Schuller.—The author has succeeded, by using quartz vessels, in showing the volatility of certain metals below their melting points. Commercial silver in the solid state, for example, is volatile. The sublimed silver shows the characteristic colour of thin films. The lead which it may contain is volatilised first. Copper also can be sublimed with ease. Gold, of which the volatility is very slight, can be volatilised, however, in small amounts when heated up to its melting point, or to a slightly higher temperature. Tin is a little more volatile than gold. Chloride of sodium is volatilised easily without the vessel being attacked; sulphide of silver is more volatile than silver. With sulphide of lead the sublimation is so rapid that we cannot arrive at complete fusion.—*Zeit. Anorg. Chem.*, vol. xxxvii., p. 69.

The Non-precipitation of Magnesium by Ammonia in the presence of Ammoniacal Salts.—E. P. Treadwell.—The researches of the author confirm those of Loven. The non-precipitation is not due to the formation of complex ions, but to the slight dissociation of the ammonia in the presence of ammoniacal salts. The solution of chloride of magnesium precipitates about half the base immediately in the presence of a large excess of ammonia. After twenty-four hours, the precipitate contains 80 per cent of the total magnesia. With a smaller excess of ammonia, in twenty-four hours only half the magnesia is precipitated, while the precipitate separated immediately after its formation contains only one-fifth of the magnesia. Further, the cryoscopic determinations made by the author leave no doubt as to the non-existence of complex ions. The precipitation of salts of manganese by ammonia is in every respect identical with that of magnesia.—*Zeit. Anorg. Chem.*, vol. xxxvii., p. 326.

The Behaviour of Compounds of Tellurium when Heated with Hydrochlorate of Ammonium.—A. Gutbier and F. Flury.—Tellurous anhydride, tellurous acid, or the alkaline tellurites, when heated with chloride of ammonium, give a white sublimate, while at the same time the non-volatile portion of the mass becomes yellow in colour. After a certain time the residue becomes black, while at the same moment a sublimate of a yellow colour appears in the volatilised portion. By raising the temperature we obtain eventually a black sublimate. The white sublimate consists partly of AmCl . The author has also recovered from it the products of decomposition of the compound $\text{TeO}_2 \cdot 2\text{HCl}$ (Ditte, *Ann. Chim. Phys.*, [5], vol. x., p. 82); that is to say, of the tetrachloride and of the anhydride, TeO_2 . As for the black sublimable product, it represents an ammoniacal compound analogous to that described by Espenschied, $\text{TeCl}_2 \cdot 2\text{NH}_3$ (*Journ. f. Prakt. Chim.*, vol. lxxx., p. 429). The author has not observed the formation of nitride of tellurium. By replacing the AmCl with other ammoniacal salts, such as the nitrate, carbonate, sulphate, phosphate, acetate, or molybdate of ammonium, or with other chlorides, such as KCl , NaCl , or the chlorides of phosphorus, no reaction is observed.—*Zeit. Anorg. Chem.*, vol. xxxvii., p. 152.

MEETINGS FOR THE WEEK.

- TUESDAY, 17th.**—Royal Institution, 5. "Structure of Animals," by Prof. L. C. Miall, D.Sc., F.R.S.
- WEDNESDAY, 18th.**—Chemical, 5.30. "Nitrogen Halogen Derivatives of the Sulphonamides and Sulphonalkylchloro-amides," Part II., Sulphondibromamides and Sulphonalkylthioamides," by F. D. Chattaway. "Electrolytic Oxidation of Aliphatic Aldehydes," by H. D. Law. "Diazo-derivatives of the Benzenesulphonyl-phenylendiamines," by G. T. Morgan and F. M. G. Micklethwait. "Molecular Condition in Solution of Ferrous Potassium Oxalate," by S. E. Sheppard and C. E. K. Mees. "Formation of Magnesia from Magnesium Carbonate by Heat, and the Effect of Temperature on the Properties of the Product," by W. C. Anderson. "Transformations of Derivatives of *s*-Tribromodiazobenzene," by K. J. P. Orton. "Addition of Sodium Bisulphite to Ketonic Compounds," by A. W. Stewart.
- Society of Arts, 8. "Wireless Telegraphy and War Correspondence," by Capt. L. James.
- Microscopical, 8. Annual Address by the President, "What were the Carboniferous Ferns?"
- THURSDAY, 19th.**—Royal Institution, 5. "The Religion of Shakespeare," by Prof. Churton Collins, M.A.
- Society of Arts, 4.30. "The Gates of Tibet," by Douglas W. Freshfield, M.A.
- FRIDAY, 20th.**—Royal Institution, 9. "New Low Temperature Phenomena," by Prof. Sir James Dewar, F.R.S.
- SATURDAY, 21st.**—Royal Institution, 3. "Wat Tyler in London," by Prof. Charles Oman, M.A., &c.

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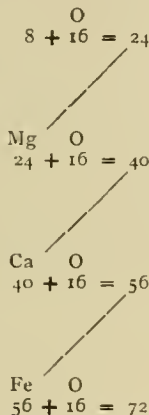
VOL. XCI., No. 2356.

A FURTHER NOTE ON THE ANOMALIES OF BERYLLIUM.

By E. W. WETHERELL, A.R.C.S.

In my previous article on this subject (CHEMICAL NEWS, xc., 260), I pointed out that the atomic weight of beryllium should be 8, and that its experimental value, 9.1, might be due to the presence of a satellite to the atom; moreover, that the "satellite" in this case was very large in comparison with the mass of the "planet" beryllium. In continuation of those observations I should like to point out a very remarkable fact.

Everyone is aware that ferrous iron, lime, and magnesia, when in combination with carbonic acid, form crystals which are isomorphous, i.e., that the three minerals, calcite, magnesite, and siderite, can have replacements to any extent, giving rise to the various minerals intermediate to them in composition. If we arrange these three oxides in the following way we see that there is an equal interval of 16 between each; that is to say, they are in arithmetical progression:—



We have here three values of the oxides, 40, 56, and 72, and since 40 and 56 also occur in the series of elements (column 1) it is probable that 72 should also occur. Now we believe that germanium (72) has an oxide, GeO (in addition to the oxide Ge_2O_3), and it is therefore not improbable that a compound, $\text{GeO} \cdot \text{CO}_2$, should be capable of existence, and if so that it should crystallise in forms isomorphous with calcite. In column 3 the first value is 24, which should be composed of Be 8 and O 16, but Be is not 8; if it were the probability is that a carbonate of beryllium with the formula $\text{BeO} \cdot \text{CO}_2$ (isomorphous with calcite) would exist, but the satellite of Be is so relatively large that it prevents the building up of forms isomorphous with those of elements which have no satellite.

I believe, therefore, that no compound with the formula BeCO_3 will be produced, and if ever it should be formed it will certainly not be isomorphous with calcite. On the other hand, I look for the formation of an artificial rhombohedral carbonate of germanium.

I now propose to show that if the "planet" barium has an atomic weight of 136 (as suggested in my previous paper), and a "satellite" of the value of 1.2, that the weights of the rhombic carbonates are also periodic, thus:—

Aragonite ..	100	(Ca = 40, O ₃ = 48, C = 12)
Strontianite ..	148	(Sn = 88, O ₃ = 48, C = 12)
Witherite ..	196	(Ba = 136, O ₃ = 48, C = 12)

Here we have intervals of 16×3 . The "satellite" of barium is relatively so small that it does not interfere to any great extent with the building up of the witherite crystals.

I pointed out that the "satellite" of zinc is probably 1.4; this would be scarcely large enough to interfere with the building up of calamine crystals, although of sufficient size to affect the physical nature of the element itself. If, then, we consider that the atomic weight of the "planet" zinc is 61, the carbonate will have the molecular weight of 124, which is exactly half way between that of siderite and that of the hypothetical germanium carbonate, and, moreover, its value 124 is likewise inter-periodic between aragonite and strontianite (i.e., in its correct position in the table of the periodic law), and also if it could crystallise in the rhombic system instead of the rhombohedral.

In the above notes I have attempted to formulate a law to the effect that in the case of certain compounds their crystal forms will be isomorphous when the atomic weights of their bases are in arithmetical progression, with intervals of 16 (simple multiples or fractions), and, furthermore, by the hypothesis of "satellites" that we should be able to predict that elements with relatively large satellites would not be able to build crystalline compounds isomorphous with those of elements whose satellites were small or entirely wanting.

Laboratory of the Agricultural Department,
Government of Mysore, India.

EUROPIUM.

By G. URBAIN and H. LACOMBE.

IN the year 1892 (*Comptes Rendus*, vol. cxiv., p. 575), M. Lecoq de Boisbaudran observed with certain samariferous solutions a spark spectrum characterised particularly by the three lines, approximately λ 466.2, 462.7, 459.3. He designated the corresponding element $\text{Z}\epsilon$. He further observed with several similar products a fluorescent band comprised between λ 622 and 611. He called the corresponding element $\text{Z}\zeta$. Since that time, Demarçay (*Comptes Rendus*, vol. cxx., p. 1019; vol. cxxii., p. 1484; vol. cxxiii., p. 1469) has isolated from the earths of this group a new earth which he designated at first Σ , and ultimately called *Europium*. Europium has the spectral characteristics of $\text{Z}\epsilon$ and $\text{Z}\zeta$. Its solutions also have a faint absorption spectrum, of which Demarçay has determined the wave-lengths.

Europium exists in very small quantities compared with samarium and gadolinium, between which it is intercalated in the series of the rare earths. Demarçay obtained it with a minimum of 18 intermediate fractions. We have succeeded in reducing this number to 3.

In previous researches (*Comptes Rendus*, vol. cxxvii., p. 792; vol. cxxviii., p. 84) we have shown that we can rigorously separate samarium and europium by taking advantage of the isomorphism and the intermediary solubility of magnesian nitrate of bismuth with the magnesian nitrates of these two earths.

The separation of europium and gadolinium is not so easy. But as the magnesian salts of europium have almost the same solubility as those of bismuth, and while those of gadolinium are decidedly more soluble, we can separate europium from gadolinium fairly easily in the tail-ends of the fractionation.

In our preparation we used 610 grms. of oxides, representing the whole of the europium earths resulting from the treatment of about 500 kilos. of monazite sands. These oxides contained principally samarium and gadolinium. The magnesian nitrates suitably treated with bismuth salts were spread out over 30 fractions. The proportion of material contained in each fraction was practically constant. The hot solution in each case had a bulk of 300 c.c., and after crystallisation left about 30 c.c. of mother-liquors

Weights.

Fraction No.	(SO ₄) ₃ Eu ₂ .8H ₂ O.	(SO ₄) ₃ Eu ₂ .	Eu ₂ O ₃ .
15 ..	1'7787	1'4303	0'8500
16 ..	2'47'5	1'9935	1'1848
17 ..	2'4777	1'9449	1'1554
18 ..	2'4831	1'9968	1'1870
19 ..	2'2988	1'8488	1'0990

Percentages.

Fraction No.	H ₂ O per cent.	SO ₄ per cent.	Eu ₂ O ₃ per cent.	Total per cent.
15 ..	19'587	32'624	47'787	99'998
16 ..	19'568	32'628	47'803	99'999
17 ..	19'555	32'655	47'789	99'999
18 ..	19'584	32'612	47'803	99'999
19 ..	19'575	32'617	47'807	99'999

Atomic Weight by the Transformation of—

Fraction No.	(SO ₄) ₃ Eu ₂ .8H ₂ O (SO ₄) ₃ Eu ₂ .	(SO ₄) ₃ Eu ₂ into Eu ₂ O ₃ .	(SO ₄) ₃ Eu ₂ .8H ₂ O into Eu ₂ O ₃ .
15 ..	151'58	151'77	151'72
16 ..	151'94	151'80	151'83
17 ..	152'17	151'61	151'74
18 ..	151'639	151'89	151'83
19 ..	151'80	151'88	151'86
Means..	151'826	151'790	151'796

The fractionation must be constantly followed up by an examination of the absorption spectrum of europium.

It was stopped when fractions 13 and 14 no longer gave any absorption spectrum, when examined through a thickness of 10 c.m., and under the existing conditions of concentration.

The number of rounds of fractionation made was 160, which represents a total of about 3000 crystallisations.

The fractions containing europium gave, after the elimination of the bismuth, the following weights of oxide :—

Order No. of fractions	14.	15.	16.	17.	18.	19.	20.	21.	22.
Weight of oxides	0'537	1'01	1'5	1'74	1'5	1'8	2'7	12'7	29

The six first fractions did not show the gadolinium lines in the electric spark, and the fractions beyond 22 no longer gave the lines of europium.

It results from the above figures that the monazite sands contain approximately two hundred-thousandths of oxide of europium.

We have not observed, up to the present, any difference in our various fractions of pure europium, and if this substance is a mixture, its components cannot be separated by the fractionation of its magnesium salts. Further, the atomic weight remains constant.

After having been precipitated by alcohol, the neutral sulphate is crystallised on the water-bath in aqueous solution. The salt thus obtained answers to the formula Eu₂(SO₄)₃.8H₂O.

It forms distinct crystals having a hardly visible rose tint. This salt, unchangeable in the air, is first dehydrated at about 375°. The anhydrous sulphate thus obtained is then calcined at about 1600°, which transforms it integrally into the oxide. The oxide thus prepared is quite rose-coloured, while the oxide prepared at a low temperature by the calcination of the oxalates is white, with an almost imperceptible rose tint in the mass.

These measurements have enabled us to calculate the atomic weight of europium :—

1. By the transformation of the hydrated sulphate into the anhydrous sulphate.
2. By the transformation of the anhydrous sulphate into the oxide.
3. By the transformation of the hydrated sulphate into the oxide.

These measurements control each other reciprocally, and give practically identical results. In any case, the transformation of the hydrated sulphate into the oxide gives the best results; in fact, the weights of the extreme terms shows no inaccuracy, and, on the other hand, the difference in the extreme weights being the greatest in this case, the relative error is necessarily very small.

The accompanying tables give our experimental results.

We conclude from these measurements that the atomic weight of europium is 151'79, and we estimate that this figure differs from the true figure by less than 0'06.

The original material for this research was very kindly given to us by MM. Chenal and Douilhet.—*Comptes Rendus*, vol. cxxxviii., p. 628.

THE COMPLEX COMPOUNDS OF ZIRCONIUM.*

By ALFRED MANDL.

IN this paper the author examines the behaviour of solutions of nitrate of zirconium with salts of the organic acids, alcohols, and pluralival phenols.

The original substances employed were the nitrate, acetate, and carbonate of zirconium. The nitrate, prepared by dissolving the oxide in nitric acid and evaporating the solution, consists of a white amorphous mass soluble in cold water. Like the commercial nitrate, it consists not only of a neutral salt, but also of a basic one. The addition of nitrate of potassium to the solution of the nitrate does not prevent the hydrolysis of the neutral salt, for by evaporation we obtain a crystalline mass containing less nitric acid than is required by the neutral salt.

The acetate is obtained easily, among other methods, by precipitating a dilute solution of nitrate of ammonia and acetate of ammonia. The precipitate obtained is then dissolved in an excess of acetic acid, and the solution evaporated on the water-bath. The residue consists of a gummy mass soluble in cold water.

The carbonate was obtained by the action of carbonate of ammonia on solutions of the nitrate in the presence of carbonic acid. It is necessary to prevent as much as possible an excess of alkaline carbonate in which the salt of zirconium is soluble.

Of the numerous compounds examined (about fifty), some behave like formic and acetic acids; that is to say, with solutions of nitrate of zirconium they give precipitates insoluble in an excess of the reagent; others, such as glycolic acid, give precipitates soluble in an excess of the reagent.

Numerous double salts are described :—

Double Oxalates, Zr(C₂O₄K)₄ + 5H₂O. — Monoclinic crystals giving solutions acid to phthalein, neutral to methyl orange.

Zr(C₂O₄NH₄)₄ + 6H₂O. — Monoclinic crystals easily soluble in cold water.

Double Malonate, Zr(CO.O.CH₂.COOK)₄ + 11H₂O. — Hygroscopic microcrystalline powder, of which the solutions decompose on boiling.

Double Malate, Zr(CO.O.CH = CH.CO.OK)₄ + H₂O. — A crystalline mass soluble in water.

Double Glycolate, Zr(C₂H₃O₃)₄ + 3H₂O. — Crystals soluble in water, giving a solution acid to methyl orange and to phthalein.

Double Malate, ZrK₃(C₃H₃O₆)₃.C₃H₆O₄ + 4H₂O.

Double Tartrates, Zr₃K₄(C₄H₂O₆)₄ + 10H₂O. — A microcrystalline powder.

Zr(CO₂K)₂(CO₂Na)₂(COH)₄. — A microcrystalline powder.

Double Citrate, Zr.C₆H₄O₇.K₃.C₆H₅O₇ + 9'5H₂O. — Monoclinic needles.

Double β-Resorcyate, (C₇H₄O₄)₃K₂Zr + 4H₂O. — Microscopic crystals very easily soluble in water.

* Abridged from the paper in the *Zeitschrift für Anorganische Chemie*, vol. xxxvii., p. 252—302.

Attempts to prepare double salts with pyrotartaric, phthalic, and gallic acids did not lead to any very definite results.

In a general way we may state that the monocarboxylic acids do not form double salts. To effect the formation of complex salts the necessary condition for the acids is the existence in the molecule of two neighbouring carboxylic groups.

For the oxycarboxylic compounds it results, according to the tables in the paper, that the acids are only dissociated very slightly, not giving double salts, or only complex salts.

The author attributes this behaviour to the connection of the zirconium with the hydroxy groups. Further, the salts of these acids have an acid reaction. The hydroxy compounds behave in the same manner as the oxycarboxylic compounds.

A CADMIUM AMALGAM LAMP OF QUARTZ.

By O. LUMMER and E. GEHRCKE.

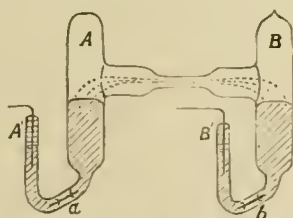
HERR GÜMLICH (*Zeit. für Instrumentenkunde*, 1897, xvii., p. 161) has employed a vacuum arc lamp filled with cadmium amalgam, which interpolates the bright cadmium lines into the spectrum of mercury. This lamp supplies a want for many purposes of optical measurements. In spite of this advantage, however, it has not yet been found possible to employ the amalgam lamp, principally because it does not last long; while a properly made mercury lamp can be burnt for years, the cadmium amalgam lamp sometimes flies in pieces after only a few experiments.

After the firm of W. C. Heraeus, of Hanau, had recently succeeded in preparing mercury lamps from quartz, the next thing to be done—Herr Gümlich has already suggested this (*Zeit. f. Instrumentenkunde*, 1904, xxiv., p. 120)—was to try if, on using a similar lamp globe made of amorphous quartz, a cadmium amalgam lamp suitable for continued use could be constructed. Our experiments show that this is actually the case.

As the filling of such a quartz lamp seems not to be limited to cadmium and other amalgams, but may possibly be extended to other easily fusible metals, *e.g.*, pure cadmium, zinc, &c., and, as, moreover, the preparation of such lamps is of great importance in spectroscopy, we propose to describe here the results we have so far obtained.

Through the kindness of the firm of W. C. Heraeus we have obtained two quartz lamps, to which, for special purposes, we have given the form shown in the accompanying figure.

Two vertical cylindrical tubes, A and B, of 1.5 c.m. diameter, are joined to form a vessel in the shape of an H



by means of a capillary of 0.2 c.m. diameter included between two wider pieces of tube. The limbs are filled with mercury or amalgam, the lower contracted end is bent twice at right angles, and each ends in a narrower tube, A' and B', of 0.5 c.m. diameter, open at the top. At a and b a piece of iridium wire is melted in, which closes the circuit of the vessels A and B. The closing is made more secure by filling the tubes A' and B' also with metal. Two iron wires which are immersed in the mercury serve as outer leads. The open ends of A' and B'

are cemented to the iron electrodes by shellac and Chatterton cement. The filling and exhausting of the lamp is easily performed by means of a quartz tube which is fused off from B; since as perfect as possible a vacuum is necessary for satisfactory burning, the tube is not fused off (from B) till the lamp has been burnt for some time, and has been powerfully heated externally in all parts by a Bunsen burner or blowpipe.

The amalgam used by us contains 14 grms. of cadmium, to 100 grms. of mercury, and at the ordinary temperature forms a soft pulpy mass, which on gentle heating becomes as liquid as mercury and which can be easily handled. The feeble oxidation occurring on filling with the heated amalgam is so slight that it has no ill effect.

The lighting of the lamp can be effected by shaking, or more conveniently by means of a match, such as is used for Hewitt's mercury lamp. The current flowing through a self-induction, arranged in parallel (110 volts), is suddenly interrupted, and then produces so high a potential that the space between the electrodes A and B is sparked across. If the arc light is set going it burns with 1 to 2 ampères more. Before exciting the current the lamp must be warmed with a Bunsen burner until sufficient vapour of the metal is present in the interior. The height of the metal in the two limbs can be regulated by inclining and shaking, and when the metal is high enough the lamp burns for hours without further heating; if it should go out, external re-warming is usually necessary.

Intense ultra-violet light, which the quartz vessel allows to pass through, proceeds from the lamp as well as visible rays. We usually burn the lamp in a box of copper foil provided with glass windows, in order to do away with the danger of the ultra-violet rays affecting the eyes, as well as with the odour of ozone.*

The light emitted by the lamp contains the following bright wave-lengths of the visible spectrum:—

	Cd.	Hg.	Hg.	Hg.	Cd.	Cd.	Cd.	Hg.
λ	644	579	577	546	509	480	468	436 μ

The intensity of the lines varies according to the conditions under which the lamp is burnt; also, the colour of the light emitted varies from whitish-blue to greenish-white. The mercury lines, especially 546 μ , are the brightest, but the cadmium lines, principally 509 μ , are of very considerable brilliancy. Most light is emitted in the direction of the capillary; in this direction the brightness of the cadmium lines is too great for the eyes to endure.

On taking an observation in our interference spectroscopy, with a plane parallel plate of thickness 0.5 c.m. and length 20 c.m., the mercury lines—corresponding to the high vapour pressure in the interior of the lamp—were fainter than in the lamp construction described by one of us (O. Lummer, *Zeit. f. Instrumentenkunde*, 1901, xxi., p. 201); also, the satellites of the lines, especially on strong cooling, develop more brilliantly in the latter. The cadmium lines, though they possessed the same satellites, showed a simpler structure than the mercury lines. The lines 509 and 480 μ had each five satellites, while the red line 644 μ , in agreement with Michelson's results (*Trav. et Mém. du Bureau Intern. des Poids et Mesures*, 1895, xi., p. 143) possessed the simplest structure, but yet showed an asymmetrical complex (three-fold) structure (O. Lummer, *Zeit. f. Instrumentenkunde*, 1901, xxi., p. 201). The satellites of the cadmium lines do not, however, exhibit such a constant phenomenon as those of the mercury lines; according to the movements and variations of the arc light they appear with different intensity and in different places in the interference spectrum. When the lamp was burnt under certain conditions, accidentally occurring for a short time, the line 644 and also

* The smell of ozone is, moreover, greater with a lamp filled with mercury than with the amalgam lamp.

509 μ showed no satellites; the strength of the light was then by no means small. Herr Fabry (*Comptes Rendus*, 1904, cxxxviii., p. 854) has also observed variations of the satellites of the cadmium lines. This fact seems to us to be of some significance in the use of these lines as normals of the standard of length.

As regards the durability of the cadmium amalgam lamp there seems no reason why this should be limited; in the lamp described by us, however, a deterioration in the burning occurred in time, inasmuch as at first we had to heat less strongly in order to set the arc lamp going; also, the lamp went out more frequently after a time, and it was found best to heat continuously during the burning with a Bunsen burner; then the lamp burnt as long as required. We are uncertain whether this deterioration is connected with a development of occluded gas from the metal, or whether the small quantity of yellowish oxide deposited on the walls plays a part in it; but when the lamp was again exhausted and heated it acted as well as at first.—*Zeit. f. Instrumentenkunde*, 1904, xxiv., p. 298.

METHODS FOR THE DETECTION OF ACETATE, CYANIDE, AND LITHIUM.

By STANLEY R. BENEDICT.

A METHOD for the detection of acetates, much more delicate than those in common use, or than any of which I have been able to find record, can be based upon the two well-known facts (1) that, unlike most weak acids, acetic acid has a soluble silver salt, and (2) that the acidity or degree of ionisation of acetic acid is greatly reduced by the presence of an acetate.

The solution, freed from all cations except those of the sodium group, is made just alkaline with sodium carbonate. An excess of silver nitrate solution is now added and the precipitate filtered off, the solution being thus left perfectly neutral. The excess of silver is removed with a little normal sodium chloride solution. The filtered solution is now saturated with hydrogen sulphide.

In another test-tube 2 c.c. normal cobalt nitrate are acidulated with 2 or 3 drops normal acetic acid and saturated with hydrogen sulphide. A small amount of cobalt sulphide will usually be precipitated, but may be disregarded.

Upon mixing the two solutions thus prepared a heavy black precipitate of cobalt sulphide will be obtained immediately if the test solution contains acetate. This test is capable of detecting acetate in a N/500 solution of sodium acetate. It is applicable in presence of all strong acids and of all weak acids having insoluble silver salts.

The following method for the detection of cyanides in presence of sulphocyanates and ferrocyanides is reliable and extremely delicate. It has the advantage over the best methods hitherto proposed of avoiding the somewhat cumbersome expedient of distillation. It is based upon the action of cyanides upon the freshly precipitated oxides of mercury. As the method was first worked out, a solution of the mercuric salt was made alkaline with sodium hydroxide and the solution to be tested was added. It was found that in presence of cyanide the yellow precipitate of mercuric oxide dissolved (presumably with formation of a complex cyanide). Neither sulpho- nor ferrocyanides show this solvent action upon mercuric oxide.

The solvent action of cyanides is so marked that a portion of the precipitate formed, upon treating 1 c.c. of N/25 mercuric chloride solution with sodium hydroxide, can be seen to dissolve when treated with a few cubic centimetres of a N/2000 solution of potassium cyanide. Of course, the full delicacy of the test could best be secured by filtering off any precipitate remaining after adding the solution to be tested, acidifying the filtrate, boiling, and testing for mercury with hydrogen sulphide.

It has, however, been found, that the action of cyanides upon mercurous oxide can be made the basis of a more delicate and desirable test than the one above proposed.

If a solution of mercurous nitrate be precipitated with an excess of sodium hydroxide, and potassium cyanide solution then be added, a portion of the precipitate dissolves, while the colour of that which remains is changed from black to light grey. The action of the cyanide is to cause a portion the mercurous oxide to be reduced to metallic mercury with the formation of a corresponding amount of mercuric oxide, which is then dissolved by the cyanide present. The grey precipitate remaining can readily be shown to be metallic mercury. O. Vitali (*L'Orosi*, xv., 186; *Journ. Chem. Soc.*, 1892, lxiii., 1416) showed that hydrocyanic acid has this action upon calomel and some other mercurous salts. The mercurous oxide is in nowise affected by either ferrocyanides or sulphocyanates. In order to obtain the full delicacy of the test it should be made as follows:—

The solution to be tested is made alkaline with sodium hydroxide, then about 0.5 to 1 c.c. of N/25 mercurous nitrate is allowed to flow slowly down the side of the tube so that it will remain upon the top. A ring of black mercurous oxide is thus formed. The test-tube is now gently agitated so that a mixture of the precipitate with the solution slowly takes place. If cyanide be present, a portion of the precipitate will dissolve while the rest will become light grey in colour.

When made as above described this test is extremely delicate, readily detecting CN in 5 c.c. of a solution containing about 1 part CN in 1,000,000 parts of solution. This is not the limit of its delicacy. When it is remembered that the limit of the Prussian blue test for cyanide is placed by Link and Moeckel at 1 part in 50,000, it will be seen that this test is not at all lacking in delicacy (Link and Moeckel, *Zeit. Anal. Chem.*, 1878, xvii., 456).

When the test is made, not by the contact method as described, but by simply adding the mercurous nitrate to the alkaline test solution, there is a possibility, when the proportion of mercurous nitrate used is small, of mistaking the small quantity of black mercurous oxide, distributed through the liquid, for the grey mercury, whose formation constitutes the test, but no such confusion can arise if the above directions are adhered to. For the most delicate work a blank test with pure sodium hydroxide may be made for comparison, the same proportions of mercurous nitrate and sodium hydroxide being used as in the test.

While ferrocyanides would interfere with this test, it will be remembered that cyanides are oxidised by these, so that it is unnecessary to test for cyanides when ferrocyanides are present.

The detection of lithium in the presence of sodium without the aid of the spectroscope is attended with considerable difficulty. Of the precipitation methods so far proposed, practically only one can be of any service, viz., the precipitation as phosphate in alkaline solution. Yet this method, as hitherto proposed, can be applied only where lithium is present in considerable amount, say, not less than a N/8 solution. By the modification of this method described below, it is possible to obtain a distinct precipitate with a N/100 solution of lithium chloride, this being about the limit of its availability. This modification depends upon the fact that the precipitate of lithium phosphate is much less soluble in dilute alcohol (whether hot or cold) than in water, while sodium phosphate, although precipitated by dilute alcohol, readily re-dissolves upon heating. The procedure is as follows:—A little ammonium hydroxide is added to the solution to be tested, then about one-tenth volume of N/5 disodium hydrogen phosphate is added, and finally enough ethyl alcohol to produce a fairly heavy precipitate, which remains permanent upon shaking the tube. This precipitate may consist of only sodium phosphate, or may be a mixture of sodium phosphate and lithium phosphate. The solution is now heated to boiling. If lithium be absent the precipitate will completely dissolve, leaving a perfectly clear

solution; if, however, lithium be present it will be precipitated upon warming, and the precipitate will not dissolve even upon hard boiling. If the amount of lithium be small the solution will first clear, and the precipitate will form upon boiling. Salts of potassium and ammonium do not interfere.—*American Chemical Journal*, xxxii., No. 5.

THE ACTION OF HYDROGEN PEROXIDE UPON ANHYDRIDES, AND THE FORMATION OF ORGANIC ACID, PEROXIDES, AND PERACIDS.*

By A. M. CLOVER and A. C. HOUGHTON

(Continued from p. 21).

Action of an Aqueous Solution of Hydrogen Peroxide upon Acetic Anhydride (continued).

THE same volume of hydrogen peroxide was added to 250 c.c. of dilute sulphuric acid (2N), and again estimated. Required, 16.85 c.c.; duplicated, 16.85 c.c.

The same volume of hydrogen peroxide was added to 250 c.c. of dilute sulphuric acid (2N). 0.05 gm. of acetic anhydride was added, together with a solution of acetic peroxide, which had stood four or five hours, and was equivalent to 1 c.c. N/20 thiosulphate "immediate," and 9 c.c. total. Required, 16.85 c.c. permanganate.

The estimation of acetic peroxide in this manner is dependent upon three other determinations, each of which is liable to a reasonable experimental error. The numbers obtained are therefore approximate ones, but are all that can be desired.

The following experiments were made with the same solutions of hydrogen peroxide as were previously employed in the estimation of peracid, and were carried out in exactly the same manner, care being taken to make all conditions and measurements the same. The portion to be estimated for hydrogen peroxide was delivered into 500 c.c. of water at the proper time. Only a portion of this was titrated, the numbers appearing in the table representing the entire amount. It was not necessary to remove the portion to be estimated for total active oxygen at exactly the time indicated, as there is little variation in this value, during the time of the experiment. The figures in the table represent the amounts of N/20 solutions required by 1 c.c. of the reaction mixture:—

Hydrogen Peroxide, 61.6 Grms. per Litre.

Time in minutes.	Total thiosulphate.	Immediate thiosulphate.	Permanganate.	Thiosulphate representing peroxide.
3	68.7	1.0	66.95	0.75
6	68.8	1.35	66.1	1.35
18	68.7	1.9	64.4	2.4
30	68.9	2.6	64.2	2.1

Hydrogen Peroxide, 45.4 Grms. per Litre.

3	51.0	0.7	49.9	0.4
6	50.8	0.9	48.1	1.8
18	50.8	1.3	46.65	2.85

Repetition of these experiments a number of times gave values which varied within a comparatively narrow range for reasons already mentioned. In no case, however, were the numbers found to exceed those given by more than 1.0.

Experiments were made to determine the rate of hydrolysis of acetic peroxide in a solution of hydrogen peroxide. The solutions of hydrogen peroxide used were the same as in the previous experiments. A solution of acetic peroxide (approximately N. 5) was made by dissolving 1.2 grms. of pure acetic peroxide in 100 c.c. of hydrogen peroxide. This concentration of acetic peroxide is considerably greater than that at any time in either of the

solutions examined. The temperature remained at 21°. The peracid in 1 c.c. of the solution was estimated at intervals in the usual manner. The amount is represented in the tables below by N/20 thiosulphate, column I, representing the stronger solution of hydrogen peroxide and column II, the weaker:—

Time in minutes.	I.	II.
2	0.2	0.2
4	0.3	0.3
8	0.45	0.4
16	0.8	0.6

These numbers are to be compared with those obtained for peracid in the previous experiments. It is evidently impossible to account for the amount of peracid in those solutions, assuming that it is formed by the hydrolysis of acetic peroxide. The comparison applies especially to the earlier stages of the reaction. It is known that later acetic peroxide is formed in considerable amount, and that this eventually hydrolyses to peracid.

To make sure that the acetic acid present in the original experiment had no accelerating action on the rate of hydrolysis of the peracid, the reactions were compared in hydrogen peroxide solution of about 5.5 per cent, and in a 10 per cent acetic acid solution, containing the same concentration of hydrogen peroxide. The same amount of pure acetic peroxide was added to each solution. The amounts of peracid formed at intervals in 1 c.c. of the solutions as represented by N/20 thiosulphate are given below:—

Time in minutes.	Acetic acid solution.	Unacidified solution.
20	0.3	1.1
40	0.6	1.8
60	0.8	2.3

It will be seen that the acid has a retarding rather than an accelerating influence.

It is evident that acetic peracid results directly from the action of acetic anhydride upon hydrogen peroxide, probably according to the following equation:—



This reaction is analogous to that of acetic peroxide upon hydrogen peroxide, already considered. Here again, we must notice the similarity between the action of hydrogen peroxide and ordinary hydrolysis by means of water.

One of us has previously shown (*loc. cit.*) that peracids, even in very dilute solutions, are extremely reactive toward substances capable of ordinary hydrolysis. It was shown that either benzoic or acetic peracids could be almost completely converted into benzoic acetic and acetic peroxides respectively, even in very dilute aqueous solution, by the addition of a small amount of acetic anhydride to the solution. The formation of the peroxide is therefore to be explained by the action of peracid upon unchanged anhydride. The great tendency for these substances to react is seen in the sudden check in the rate of formation of peracid during the reaction of acetic anhydride upon the solution of hydrogen peroxide.

Propionic anhydride was also found to show the same general behaviour toward hydrogen peroxide as acetic anhydride. Its action is slower, but on account of its sparing solubility it is less suitable for study.

Since acetic peroxide is almost completely changed to peracid in the course of twenty-four hours, experiments were made to determine the practicability of preparing a solution of acetic peracid by allowing a solution of anhydride in hydrogen peroxide to stand for this length of time.

1. Two c.c. of acetic anhydride were added to 100 c.c. of a 3.2 per cent commercial hydrogen peroxide solution, and kept cool by immersing in a vessel of water. After twenty-four hours the total amount of peracid in the solution estimated in the usual manner was 0.33 gm. From this

* From the *American Chemical Journal*, xxxii., No. 1.

it follows that about 22 per cent of the anhydride entered into reaction with hydrogen peroxide.

2. Five c.c. of acetic anhydride were added to 100 c.c. of the same hydrogen peroxide solution, and kept cool. After twenty-four hours the solution contained 0.82 grm. peracid. Here again, 22 per cent of the anhydride entered into combination with the hydrogen peroxide.

3. Ten c.c. of anhydride were added to 100 c.c. of the same hydrogen peroxide solution, and kept cool. After twenty-four hours there were 1.54 grms. of peracid in the solution. In this case 21 per cent of the anhydride entered into reaction with the hydrogen peroxide.

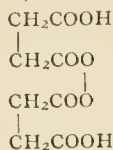
These experiments bring out an important fact; namely, that the rate of the reaction of hydrogen peroxide with anhydride is much greater than that of water with anhydride. From the relative concentrations of the two substances in the above solutions it might be expected that if the rates were nearly equal, only a little over 3 per cent of the anhydride would have reacted with the hydrogen peroxide. The fact that about the same per cent was obtained in the three experiments shows that the acetic acid has little influence upon the relative rates. An excess of hydrogen peroxide was present in each experiment. In the third only a little over 20 per cent of the hydrogen peroxide was used, and in the others much less. The secondary reaction of anhydride upon peracid would only tend to destroy the anhydride, and decrease the yield of peracid, as the active oxygen remains the same after this reaction.

A much better yield of peracid may be obtained by using a stronger solution of hydrogen peroxide, easily obtained by concentrating in a vacuum.

Twenty c.c. of a solution of hydrogen peroxide containing 104 grms. per litre were added to 6.1 grms. of anhydride, and the mixture shaken and kept cool until the anhydride had gone into solution. It was then allowed to stand in a vessel of water for twenty-four hours. At the end of this time hydrolysis was complete, and the solution contained about 2 grms. of peracid, about 45 per cent of the theoretical yield.

Anhydrides of Dibasic Acids.

Succinic Peroxide Acid,—



—When a 3 per cent solution of hydrogen peroxide is saturated with succinic anhydride, the oxidising power of the solution rapidly changes, as can be noted by its effect on potassium iodide. The products of the reaction remain dissolved, however, as there is no precipitation from the solution. If a stronger solution of hydrogen peroxide be employed and excess of anhydride be added, and the mixture shaken, so as to keep the solution saturated with the anhydride, a precipitation soon occurs. The anhydride used was in the form of broken pieces of a solid product, and after agitation it quickly settled to the bottom of the vessel. The precipitate consists of very fine crystals, and remains suspended in the liquid. After a considerable quantity had formed it was filtered, washed several times with water, dried quickly by packing tightly on a porous plate, then pulverised, and allowed to remain in a vacuum for several hours. For analysis it was re-crystallised from acetone. The active oxygen was estimated by dissolving the substance in a small amount of water, adding an excess of potassium iodide, and titrating at once with standard thiosulphate.

0.2383 grm. substance gave 0.3563 grm. CO_2 and 0.0871 grm. H_2O .

0.1232 grm. substance required 20.82 c.c. N/20 thio-sulphate.

	Calculated for $\text{C}_4\text{H}_4\text{O}_6$	Found.
C	41.00	40.78
H	4.31	4.10
O (active)	6.84	6.78

The amount of succinic acid present in the substance after complete hydrolysis and removal of active oxygen was determined and found to agree with the theoretical.

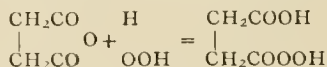
The substance was covered with about 20 parts of water in a test-tube, a pinch of platinum black added, and allowed to stand for a week. The succinic acid formed was then estimated by titrating with N/10 potassium hydroxide.

0.1954 grm. substance required 33.25 c.c. N/10 KOH.
Calculated, 33.40 c.c.

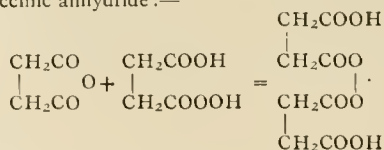
0.1290 grm. substance required 22 c.c. N/10 KOH.
Calculated, 22.05 c.c.

The substance is moderately soluble in water, alcohol, acetone, and acetic ether; sparingly in ether; insoluble in chloroform, benzene, and legroin. It is colourless, and, when pure, odourless. The crystals are flat plates, generally very irregular. The substance begins to soften at 115° , and is completely melted at 128° with decomposition. When brought into a flame it explodes; it does not explode on percussion or friction. When openly exposed to the air it slowly deteriorates, but when well stoppered no deterioration could be detected after several months.

Assuming the action of succinic anhydride upon hydrogen peroxide to be similar to that of acetic anhydride, the first step is the formation of succinic monoperacid,—



At the same time a certain amount of anhydride undergoes ordinary hydrolysis with water with the formation of succinic acid. The strength of the hydrogen peroxide solution employed determines the proportion in which the anhydride enters into each of these reactions. Succinic monoperacid is very soluble in water, and does not separate from the solution. The second step in the formation of the peroxide acid is the action of succinic monoperacid upon succinic anhydride:—



The best yield of the peroxide acid is obtained by employing a 7.5 to 8 per cent solution of hydrogen peroxide.

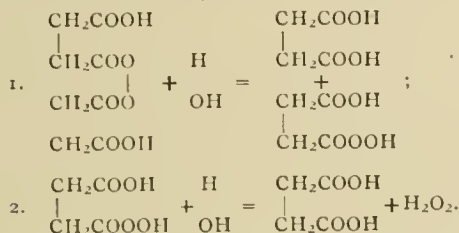
Ten grms. of ordinary crystalline succinic anhydride were added to 25 c.c. of 7.5 per cent hydrogen peroxide, and the mixture shaken. The temperature, gradually rose, but was kept below 30° . At the end of thirty-five minutes there was no further rise in temperature, indicating that all anhydride had been dissolved. The product was then filtered and washed several times with small portions of water. It was then packed tightly on a porous plate, placed in a warm place, and after an hour was perfectly dry. An analysis showed the substance to be pure. Yield, 7.5 grms.

When excess of the peroxide is added to water and shaken the amount dissolved gradually increases. This increase is due to the hydrolysis of the dissolved peroxide, which takes place according to the laws previously developed (*loc. cit.*). The rate of the reaction is much greater than that with any peroxide previously studied.

An excess of finely pulverised peroxide was continuously shaken with water at about 24° . At intervals of five, ten, fifteen, and twenty-five minutes a small portion of the mixture was filtered, and the amount of peroxide dissolved was

determined. At the end of five minutes the solution contained 19.8 grms. per litre; at the end of ten minutes, 21.5 grms per litre; at the end of fifteen minutes, 28.4 grms. per litre; and at the end of twenty-five minutes, 35.8 grms. per litre. At this rate of hydrolysis, the original solubility may be placed approximately at 15 grms. per litre. At the end of fifteen minutes the original solubility is almost doubled.

A large excess of peroxide was added to water in a beaker and kept stirred continuously for several hours. The rate of hydrolysis as indicated by the active oxygen content of the solution was found to decrease as the solution became stronger. At the end of one-half hour hydrogen peroxide could easily be detected in the solution by means of the titanous or chromic acid tests. After six hours an appreciable portion of the active oxygen of the solution (over 0.5 per cent) was present as hydrogen peroxide. By this means it was possible to obtain a very strong solution of the products of hydrolysis. The substance hydrolyses according to the following equations. The second change is much slower than the first:—



Succinic peroxide acid presents a striking difference from other bodies of the peroxide type in the behaviour of the unhydrolysed substance toward potassium iodide. The action of the peroxide, as well as its hydrolytic product upon potassium iodide, is almost immediate, so that the substances cannot be distinguished from each other as could the peroxides and peracids of monobasic acids. When an excess of potassium iodide is added to a fresh saturated solution of the peroxide acid, or to the same solution after standing an hour, and which would therefore be mostly hydrolysed, the calculated amount of iodine is liberated in the short time required to make the titration with standard thiosulphate. If the solution is very dilute, a minute or two is required before the liberation of iodine is complete. It was not possible, therefore, to study the hydrolysis of the peroxide acid in dilute solution. The change into hydrogen peroxide could be followed, however, by comparing the immediate liberation of iodine with the total.

The following figures indicate the gradual formation of hydrogen peroxide:—(1) In a 1 to 1000 solution, and (2) in a 1 to 100 solution:—

Time in days.	1. Per cent of active oxygen as H ₂ O ₂ .	2. Per cent of active oxygen as H ₂ O ₂ .
1	7.3	5.3
2	14.0	8.3
7	41.0	40.0

The active oxygen content of the weaker solution had not appreciably decreased at the end of one week. In the stronger solution there was a decrease of only 1.5 per cent.

In addition to its action on potassium iodide the following are interesting properties, possessed by a solution of succinic peroxide acid. A small amount of manganous salt added to the solution soon produces the deep rose-red colour of permanganic acid. The reaction is an extremely delicate test for traces of manganese. The colouration is prevented by the presence of considerable mineral acid. An excess of manganese salt gives, of course, manganese dioxide. The red solution of cobaltous salt is changed to an emerald-green, owing probably to the formation of a cobaltic salt; the solution slowly evolves oxygen. The addition of

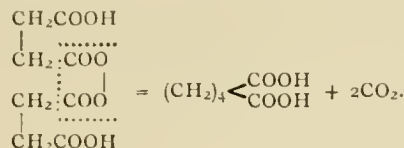
sodium acetate to the solution produces a precipitate, probably a higher oxide of cobalt. The green solution of a nickelous salt is soon changed to a purple, which is probably due to the formation of a nickelic salt. The latter seems to be unstable, however, as the solution evolves oxygen, and in the course of a few hours the purple colour disappears. The addition of sodium acetate to the purple solution causes immediate change to green with evolution of oxygen.

Finely divided manganese dioxide appears to have no catalytic action upon a solution of the peroxide acid, but is oxidised in part to permanganic acid. Lead dioxide has no catalytic action, but platinum black has a slight action. The solution has no effect upon chromic acid, titanous acid, or potassium permanganate, until it has stood an hour or more, and hydrogen peroxide has been formed.

As already stated, succinic peroxide acid, like all peroxides, decomposes when heated. The decomposition was studied by adding the substance to xylene, which was heated to its boiling-point. Carbon dioxide was evolved, the amount being a little less than 1 molecule per molecule of peroxide. Only a trace, if any, of oxygen or hydrocarbons was evolved. On cooling the xylene a crystalline product separated, which was about 50 per cent of the original weight of substance. This product consisted chiefly of succinic anhydride, which was removed by digesting with chloroform on the water-bath. The residue was distilled, whereupon water, succinic acid, and anhydride passed over. The residue from this distillation consisted chiefly of adipic acid, which was re-crystallised from water and identified by its melting-point.

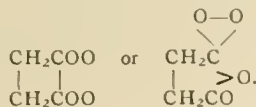
0.1204 grm. substance required 16.45 c.c. N to KOH.
Calculated for adipic acid, 16.45 c.c.

From the original xylol solution there was obtained, after removal of the solvent, a gummy residue, which dissolved completely in sodium carbonate. It was not identified. A small portion of the substance therefore decomposes as follows:—



The major portion, however, decomposes to yield succinic anhydride and the gummy acid substance already mentioned.

Vanino and Thiele (*Ber.*, xxix., 1724) have described a substance obtained by the action of succinyl chloride upon sodium peroxide hydrate, which they have called succinyl peroxide, and to which they have assigned the formula C₄H₄O₄. Baeyer and Villiger (*Ber.*, xxxiv., 762) have pointed out that the insolubility of the substance in water and in all other solvents renders improbable such a simple formula as the one assigned. We have prepared the substance according to the directions of Vanino and Thiele in order to determine the per cent of active oxygen. There is no way to purify the substance, so that the crude product, well washed and dried, was used. This product may be an individual substance or it may be a mixture. The yield obtained was very small. If the substance is covered with a 20 per cent solution of acetic acid and potassium iodide, it gradually goes into solution after six or eight hours, with the liberation of iodine. The percentage of active oxygen, so estimated, was 10.5, a correction having been made for a blank. The percentage calculated for C₄H₄O₄ is 13.8. The substance is described in Richter's "Chemie der Kohlenstoff-Verbindungen" as having either the formula—



There is certainly no ground at present for assigning any formula to the substance, even assuming that the product in question is homogeneous in composition.

(To be continued).

NOTICES OF BOOKS

The Industrial and Artistic Technology of Paint and Varnish. By ALVAH HORTON SABIN, M.S. First Edition, First Thousand. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1904. Pp. 372.

This book was written with the object of giving a correct general outline of the subject of paints and varnishes, with a brief account of their modern use and of the principles which are involved in their fabrication and application. The author has divided his subject into twenty-two chapters, in which he deals with varnishes, lacquers, and paints of all sorts and descriptions.

Varnish is the first subject taken, and in Chapter III. we come across an interesting story as to the derivation of the word, from the golden hair of "Berenice," who, in the middle of the Third Century, B.C., was the first Queen in her own right of the Macedonian nation. Successive chapters deal with linseed oil, the manufacture of varnish, Tung oil, Japans and driers, rosin, spirit varnishes, &c. Chapters XII. to XIV. are on Japanese and Chinese paints and lacquers, and make interesting reading, while Chapters XV. and XVII. deal with the important subjects of the protection of metals against corrosion, water-pipe coating, and anti-fouling paints for the protection of ship's bottoms. House, carriage, and furniture painting and varnishing, complete a useful technical work, well written in a chatty style, well printed and illustrated, and provided with a good index.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxix., No. 25, December 19, 1904.

The Académie divided the Jecker Prize in Chemistry between M. FREUNDLER, M. MINGUIN, and M. LESPIEAU.

M. Freundler's chief researches were on:—1. The variation of the rotatory power in the homologous series of tetra-substituted tartaric ethers. These investigations he afterwards extended to the derivatives of β -methyladipic acid. 2. Investigations on the formation and properties of azoic substances and the mechanism of the reduction of nitrated derivatives in alkaline solution. 3. Researches of less importance, amongst which were the preparation of the aldehydes by means of a zinc-copper hydrogen couple, the decomposition of bisulphate combinations by alkaline nitrites, &c.

The chief work of M. Minguin for the past five years has been on the subject of camphor, borneol, and their derivatives. The first portion of this series of researches consisted in the preparation of the alcoyl-camphocarbonic ethers which, on saponification and expulsion of carbonic acid, yield alcoyl-camphors. He afterwards succeeded in producing nitric derivatives of cyano-camphor. Besides these personal investigations, M. Minguin, in collaboration with others, has effected the transformation of camphocarbonic acid into homocamphoric acid, the preparation of isomeric methylcyano-camphors, benzylidene-camphors, and bromobenzyl-camphors with their numerous derivatives,

besides investigations on the hydrogenating action of sodium alcoholates on desoxybenzoin, benzophenone, and anthraquinone.

M. Lespiau, whilst unsuccessfully endeavouring to prepare the two dibromopropylenes 1.3, brought about the synthesis of the two alcohols corresponding to these two compounds, and afterwards the two series of ethers. In addition to this work, he has also performed a very successful series of physico-chemical researches on cryoscopy, ebullition, and osmotic pressure.

The Cahours Prize in Chemistry was divided between M. Chavanne, M. Kling, M. Binet, and M. Jassoneix.

Bulletin de la Société Chimique de Paris.

Series 3, vol. xxxi., No. 6.

Research on the Decomposition of the Alkaline Earthy Carbonates by Chloride of Ammonium in the presence of Water.—H. Cantoni and G. Goguelia.—Already inserted in full.

Action of Copper on Chloric Acid, with and without the Help of Electrolysis.—André Brochet.—Already inserted in full.

The Formation of Basic Salts of Copper under the Influence of Electrolysis.—André Brochet.—Already inserted in full.

Basic Chlorate of Copper.—André Brochet.—Already inserted in full.

The Electrolysis of the Alkaline and Alkaline Earthy Chlorates with an Anode of Copper.—André Brochet.—Already inserted in full.

The Colorimetric Estimation of Chromium.—A. Moulin.—Already inserted in full.

Contribution to the Study of the Action of Chromic Acid on Diphenylcarbazine.—A. Moulin.—In this research the author used the solution of diphenylcarbazine already described in the previous paper. This solution, when treated with more or less concentrated solutions of chromic acid, gave different tints according to the degree of concentration of these solutions and the amount of reagent used. He obtained various compounds, which he calls provisionally the violet, the grey, and the brown compound. The violet compound was obtained by adding 400 c.c. of the solution of diphenylcarbazine to a solution of 1 grm. of chromic acid in a litre of water. An intense violet colour is formed at once; it is left for some hours, and the coloured material extracted with chloroform. The chloroformic solution is allowed to evaporate, and a product is left adhering to the sides of the glass in the form of violet plates. This substance is purified by solution in alcohol and the addition of a large quantity of water; after some days a very light abundant violet-coloured precipitate is deposited; this is filtered, washed, and dried *in vacuo* over sulphuric acid. If instead of adding the solution of diphenylcarbazine to a very dilute solution of chromic acid we pour it into a more concentrated one, the reaction is entirely changed, and the compounds obtained are absolutely different from the previous ones. Twenty grms. of chromic acid are dissolved in a litre of water, and 400 c.c. of the solution of diphenylcarbazine are added; first a violet tint appears, but this soon goes, giving place to a blackish brown colouration; at the same time a large amount of gas is given off. When left to stand, a voluminous brown precipitate is deposited; this can be separated by filtration, and is then washed several times with boiling alcohol until the washings are colourless. The precipitate is then dried. The alcohol used for washing the last substance is almost completely distilled off, and on cooling a precipitate is formed; this is collected on a filter, and washed with distilled water. A chloroformic solution is made, from which the purified substance is crystallised; it forms deep reddish-grey plates. The

author also describes the properties, and gives the analysis of these three substances.

Method for the Synthesis of the Aldehydes.—A. Behal and Marcel Sommelet.—Already noticed.

Action of Dehydrating on Oxypivalic Acid.—E. E. Blaise and L. Marcilly.—The acid alcohols give different products by dehydration, according to the position occupied by the alcoholic function with regard to the acid one. The primary α -dialcylised β -oxyacids cannot be dehydrated normally; thus it is of interest to know how they behave with dehydrating agents, and whether they would give lactides, lactones, and other products. The authors first tried the dehydration of oxypivalic acid by heat. By heating 11.8 grms. of this acid for six hours to a temperature of 200° in an oil-bath it was found to have lost 1.6 grms. of water. The product was insoluble in everything except boiling acetic acid. By treatment with ether a portion was dissolved, and the residue had a melting-point of 165°. Other experiments were made on the dehydrating action of sulphuric acid and the hydrazides on oxypivalic acid, and the complete decomposition of oxypivalic acid by heat.

$\alpha\alpha$ -Methylethylhydracrylic Acid.—E. E. Blaise and L. Marcilly.—The $\alpha\alpha$ -methylethylhydracrylic acid was obtained by the method already described. Methylethylacetic acid was prepared by M. M. Conrad and Bischoff's method. The methylethylmalonic acid obtained gave by distillation a very impure methylethylacetic acid; starting from 1000 grms. of malonate of ethyl, the authors obtained by fractionation:—(1) About 70 grms. of isobutyric acid; (2) 356 grms. of methylethylacetic acid; and (3) about 50 grms. of diethylmalonic acid. Thus the three expected acids were obtained. The authors have also attempted to decompose $\alpha\alpha$ -methylethylhydracrylic acid into its active components, but the results obtained were not sufficiently definite to enable any conclusions to be drawn.

New Derivatives of the Cyanacetic Ethers.—C. Schmitt.—Already noticed.

New Method for the Synthesis of the Isoxazols.—C. Moureu and Maurice Brachin.—Already noticed.

Burette for Automatic Filling up to Zero; Model by which the Unused Liquid will run back into the Flask.—M. Alvergnyat-Chabaud.—This ingenious instrument cannot well be described without the accompanying diagram.

Diethylisosuccinic Acid.—A. L. Lumière and P. Perrin.—While examining the therapeutic properties of polyethylised compounds, the authors prepared a new acid, which they call diethylisosuccinic acid. One atom of sodium is dissolved in ten times its weight of alcohol, one molecule of malonate of ethyl is added, and one molecule of iodopentane, $C_2H_5-CH.I-C_2H_5$. The mixture is then boiled for a few hours. After driving off the alcohol, the residue is treated with water. The oily layer obtained is dried over chloride of calcium, and rectified. A liquid boiling at 242–245° is separated, which is the diethyl ether of diethylisosuccinic acid, $C_2H_5>CH-CH<\begin{smallmatrix} CO_2-C_2H_5 \\ CO_2-C_2H_5 \end{smallmatrix}$. To isolate the acid, this ether is boiled with the calculated amount of baryta water, the barium salt which is only slightly soluble is separated and then decomposed by the theoretical amount of sulphuric acid. On evaporation of the filtrate we obtain a syrupy product which soon crystallises in large transparent tablets, and is the diethylisosuccinic acid, $C_2H_5>CH-CH<\begin{smallmatrix} CO_2H \\ CO_2H \end{smallmatrix}$, fusible at 52–53°. The anilide, $C_2H_5>CH-CH<\begin{smallmatrix} CO-NH-C_6H_5 \\ CO-NH-C_6H_5 \end{smallmatrix}$ obtained by heating the ether with aniline, is a substance crystallised in small colourless needles. It is insoluble in water, slightly soluble in alcohol, and fuses at 219–220°.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxvii., No. 17, 1904.

Action of Acetylene on Mercuric Chloride Solutions.—K. A. Hofmann.—If pure acetylene gas is led through an ice-cold solution of mercuric chloride and the equi-molecular quantity of sodium chloride in water for thirty minutes, and the precipitate which thus forms gradually is filtered off, washed with ice-cold water, and dried with alcohol and ether, a white powder is obtained which contains more chlorine than is present in trichlor-mercuric aldehyde, but otherwise resembles this compound in its behaviour. If the quantity of sodium chloride is increased the yield decreases, and an excess of sodium chloride prevents the precipitation of mercuric chloride by acetylene gas. From an aqueous solution of sublimate in the absence of sodium chloride almost pure trichlor-mercuric aldehyde is precipitated.

Hydrazine Carbonic Acid.—R. Stollé and K. Hofmann.—On leading carbon dioxide into a fairly strong, well cooled aqueous solution of hydrazine, $NH_2NHCOOH$ separates out as a white powder which can be obtained in the pure state by drying over sulphuric acid in an atmosphere of carbon dioxide. At 90° it gives up CO_2 and yields hydrazine carbonic acid hydrazine, $CH_5O_2N_2$, which may also be prepared by saturating a hydrazine solution with carbon dioxide and distilling in a current of carbon dioxide at the ordinary or diminished pressure. It is a viscous, clear liquid, which yields crystals after a time. These melt at 70°, are very hygroscopic, and dissolve in water without decomposition. On heating to 140 in a closed tube the compound yields some carbo-hydrazide. When heated with chlor sulphonic acid ethyl ester it gives hydrazine disulpho acid, as well as some of the mono compound. The hydrazine carbonic acid and its hydrazine salt may advantageously be used for the preparation of anhydrous hydrazine by distilling cautiously over calcium or barium oxide.

Chlorides of Sulphur.—Otto Ruff.—Physico-chemical researches have shown that a sulphur tetrachloride exists, but do not prove the existence of a dichloride. The author has now examined chemically the formation of double compounds of sulphur tetrachloride and of the hypothetical dichloride. He found that this dichloride always behaves chemically like a strongly dissociated solution of the tetrachloride in sulphur subchloride, and is thus not a chemical compound. He never obtained compounds of sulphur dichloride, the supposed compounds of SCl_2 and $SbCl_5$ and $AsCl_3$ and the iodine compound to which Jaillard gave the formula ICl_3SCl_2 being really tetrachloride compounds. The sulphur tetrachloride for these experiments was made by the slow union of S_2Cl_2 and liquid chlorine in a closed tube. It is a yellowish white substance, melting at -30.1 or -31°, giving a red liquid. It is decomposed by water almost quantitatively, giving sulphurous acid. Antimony pentachloride-sulphur tetrachloride, $SbCl_5.SCl_4$, is prepared by the addition of sulphur chloride with 68.9 per cent chlorine to a solution of antimony pentachloride in sulphuryl chloride in the cold. Analysis gave the formula $SbCl_5.SCl_4$. It forms fine white crystalline needles easily decomposed by water. In an atmosphere of chlorine it melts in a closed tube at 125–126°, and begins to sublime at about 150°. On heating in air it yields S_2Cl_2 , Cl , and $SbCl_3$. The corresponding compound $PCl_5.SCl_4$ could not be prepared. Titanium tetrachloride-sulphur tetrachloride, $TiCl_4.SCl_4$, is prepared similarly. It has to be filtered in an atmosphere of chlorine, as it decomposes very readily. It is soluble in sulphuryl chloride, chloroform, carbon disulphide, and petroleum ether; melting-point 62–64°. It sublimes at 100°, and does not decompose on heating in a closed tube filled with chlorine. Fine yellow crystals of tin tetrachloride-sulphur tetrachloride, $SnCl_4.2SCl_4$, are prepared by cooling a mixture of freshly prepared sulphur chloride with 68.9 per cent chlorine and freshly distilled stannic chloride. It is strongly hygroscopic; melting-point 37°. It decomposes at 40°, the products

of decomposition again combining on cooling to form yellow prismatic tablets, which are strongly refracting. A similar zirconium compound is formed, but is so unstable that the author could not isolate it. Ferric chloride-sulphur tetrachloride, $\text{FeCl}_3 \cdot \text{SCl}_4$, is prepared as a yellow crystalline precipitate by the addition of freshly distilled sulphur chloride with 68.9 per cent chlorine to a solution of ferric chloride in phosphorus oxychloride. Incidentally the author prepared a new compound, $2\text{FeCl}_3 \cdot \text{POCl}_3$, as a light yellow crystalline mass by dissolving freshly sublimed ferric chloride in freshly distilled phosphorus oxychloride and filtering off the crystalline mass which separates out on cooling. Iodine trichloride-sulphur tetrachloride, $2\text{ICl}_3 \cdot \text{SCl}_4$, is prepared similarly to the above double compounds. A compound of arsenic trifluoride and sulphur tetrachloride is prepared by the union of its constituents in a closed tube cooled by liquid air. It is strongly hygroscopic.

Grignard's Reaction and a New Method of Preparing Magnesium Organic Compounds.—W. Tschelinzeff.—The author has proved by a series of experiments that in Grignard's reaction the ether plays the part of a catalyser. The reaction proceeds at a high temperature in the absence of any catalyser, but in the presence of a simple ether it occurs at the ordinary temperature, and moreover, the reaction proceeds more regularly, and a greater quantity of magnesium organic compound is formed. The reaction is represented by the following equations:— $\text{I. R.Hal.} + \text{R}_2\text{O} = \frac{\text{R}}{\text{R}} \text{O} < \frac{\text{R}}{\text{R}} \text{Hal.}$

$\text{II. R.Hal.} \cdot \text{R}_2\text{O} + \text{Mg} = \text{R.MgHal} + \text{R}_2\text{O}$. If to a solution of any iodide, *e.g.*, ethyl or phenyl iodide in any inert solvent, *e.g.*, benzene, toluene, petroleum ether, &c., magnesium and a few drops of a tertiary amine, such as dimethyl aniline, are added, the magnesium organic compound is formed either immediately or on warming, according to the nature of the solvent, and the concentration of the iodide, and of the catalysing amine. This reaction develops considerable heat. The theoretical quantity of the magnesium compound is often produced, and the reaction proceeds both more energetically and more quickly than Grignard's reaction, and can be used in cases in which the latter gives unsatisfactory results.

Preparation of Yellow Arsenic.—Alfred Stock and Werner Siebert.—The authors have devised an apparatus in which black arsenic can be converted quantitatively without using a solvent into the yellow variety first described by Bettendorf. The arsenic is converted into vapour in a vacuum and the vapour condensed at the temperature of liquid air. A tube of Jena glass closed at the bottom has at its lower end a small glass beaker attached by platinum wires; in this beaker is a layer of cryptol into which insulated copper wires pass, their lower ends being bent round in the form of a ring; they are connected with a four celled accumulator battery, and the resistance is regulated so that a temperature of about 400° is reached with a current of 2 to 3 amperes. Pure arsenic is placed in the space (about 2 m.m. across) between the end of the Jena glass tube and the little beaker. The glass is then sealed at a short distance from its upper open end into an elongated pear-shaped glass vessel connected with a mercury air-pump, and the whole is placed in an outer transparent Weinhold vessel containing liquid air. Then on warming the cryptol to $425\text{--}450^\circ$ yellow arsenic is precipitated on the upper part of the pear-shaped vessel. The whole operation must be conducted in a red light in a darkened room; the yellow arsenic thus prepared is very sensitive to light, it begins to change colour (becoming brown) in a few seconds when exposed to the rays of an Auer burner placed at a distance of 10 c.m., or to an electric light, in spite of the low temperature of the liquid air. Sunlight works more quickly. On removing the liquid air the temperature of the arsenic rises, and it becomes black, a change of volume occurring, as shown by the cleaving of the black fragments from the glass wall.

While this change occurs instantaneously throughout the whole mass in the warmth, at the temperature of liquid air the change caused by light takes place slowly and the layer of arsenic remains reddish-brown and transparent for some minutes even in sunlight. The authors found that during the change of yellow into black arsenic no luminescence phenomenon was to be observed. The quantity of yellow arsenic thus obtained amounted only to about one-tenth grm. in experiments lasting half to three-quarters of an hour.

Quartz Vessels for Lecture Experiments.—Emil Fischer.—Quartz flasks are specially suitable for demonstrating the formation of water from its elements in presence of platinised asbestos. They are as resistant to sudden changes of temperature and to high temperatures as platinum, possess the advantage of being transparent, and are only about one-tenth the price. They require careful handling, however, on account of the brittleness of the material and the inequality of the strength of the walls. The oxygen and hydrogen are introduced into the quartz flask by means of two porcelain tubes bent at right angles, passing through the two-holed cork, which is not affected by heat as with platinum vessels, since the quartz scarcely conducts heat at all. The rest of the apparatus does not differ from Hofmann's.

Monomethyl Tin Compounds.—P. Pfeiffer and Ida Heller.—On heating methyl iodide with stannous iodide for four hours at 160° , extracting with alcohol, filtering off the insoluble substance, and evaporating the ethereal solution, a residue is obtained. This gives long yellow prisms of methyl tin iodide, $\text{CH}_3 \cdot \text{SnI}_3$ (melting-point 85°), on taking up with ligroin, filtering, and allowing to stand. The composition of this methyl tin iodide is $\text{CH}_3 \cdot \text{Sn}^{\text{IV}} \cdot \text{I}_3$, and thus does not correspond to the double salts of tin iodide and metals which are represented by the formula $(\text{Sn}^{\text{IV}} \cdot \text{I}_3) \cdot \text{Me}$. When tin tetra-iodide and magnesium methyl-iodide are heated together in ethereal solution and water is added to the acidified product, on evaporation of the ether an oil remains behind, from which a fraction of boiling-point $175\text{--}180^\circ$ can be obtained. The aqueous liquid, by repeated addition of ether and evaporation of the purified ether extract, gives a heavy oil, from which monomethyl tin iodide crystallises in long yellow needles. From the liquid a further quantity of the fraction of boiling-point $175\text{--}180^\circ$ can be obtained. This on fractionation yields a heavy liquid of very acid odour (boiling-point $160\text{--}170^\circ$), which is almost pure tri-methyl tin iodide.

Phenyl Compounds of the Elements of the Phosphorus Group.—P. Pfeiffer, Ida Heller, and H. Pietsch.—If the trichlorides of this group are added gradually to an ethereal solution of magnesium phenyl bromide prepared from magnesium and brom-benzene, and after some hours water and hydrochloric acid are added, and the ethereal layer removed, on adding more ether and evaporating crystals of the triphenyl compounds, $\text{P}(\text{C}_6\text{H}_5)_3$, $\text{As}(\text{C}_6\text{H}_5)_3$, $\text{Sb}(\text{C}_6\text{H}_5)_3$, and $\text{Bi}(\text{C}_6\text{H}_5)_3$, are obtained. Phosphorus reacts most energetically, and bismuth the least. It is noteworthy that in this series of phenyl compounds the melting-point of the antimony compound is less than that of $\text{As}(\text{C}_6\text{H}_5)_3$, which is again less than that of $\text{P}(\text{C}_6\text{H}_5)_3$, while the melting-point of $\text{Bi}(\text{C}_6\text{H}_5)_3$ is almost equal to that of the phosphorus compound.

MISCELLANEOUS.

The Science Year Book for 1905.—This interesting publication, edited by Major B. F. S. Baden-Powell, should be obtained by all lovers of science. It contains an Almanac, Diary, Biographical Directory, List of Scientific Societies, and a Summary of the recent Progress made in Science. Among the most interesting items in this volume we may draw attention to the Astronomical, Physical, and Chemical

Notes. Though only few readers may be fairly described as astronomers, it cannot be denied that there is a great fascination for many in watching the stars, and the charts showing the positions of the principal stars and constellations at different times of the year will be of great assistance to these amateurs. The Summary of Scientific Progress contains some useful articles on astronomy, botany, chemistry, cosmical physics, engineering, electrical engineering, geography, geology, medical science, natural history, &c. There is also a glossary of recently introduced scientific terms and names, but we must observe, however, that there are some very old friends to be found in the list, such as "atom" and "ion." The biographical directory is of interest, and gives in a few words a concise biography of most of the well-known men of science, while that portion of the volume intended for use as a diary is well arranged, and allows ample space for each day's notes. The monthly calendar is ingeniously arranged to be seen through a hole cut in the front cover, the remainder of the cover serving to protect the sheet from damage.

Action of Sulphide of Carbon on Tetra-bromide of Silicon in the presence of Bromide of Aluminium. Formation of Silico-thiourea $\text{SiS}(\text{NH}_2)_2$ from Sulphobromide of Silicon, SiSBr_2 .—M. Blix.—Dry sulphuretted hydrogen gas has no action on SiSBr_4 even at boiling temperature (150°S°), but if we add a little Al_2Br_6 a lively reaction takes place at this temperature, with the evolution of HBr . If we continue then to add sulphuretted hydrogen the reaction proceeds, and is completed at the end of about five or six days. If we then distil *in vacuo* we observe that first there passes unchanged SiBr_4 , then sulphobromide of silicon, SiSBr_2 :— $\text{SiBr}_4 + \text{H}_2\text{S} = \text{SiSBr}_2 + 2\text{HBr}$. It is best to use rather a large tube to prevent obstructions; the substance is purified by re-crystallisation in CS_2 . It forms large colourless tables, fusible at 93° , boiling at 150° ($h = 18.3$ m.m.), it fumes strongly in moist air, and decomposes with violence in water. If we dissolve 2 or 3 grms. of this substance in dry C_6H_6 in large excess cooled down to 0° , and then pass NH_3 gas dried over sodium through the solution, avoiding all traces of moisture, we observe the formation of a white precipitate consisting of a mixture of silico-thiourea $\text{SiS}(\text{NH}_2)_2$ and NH_4Br , $\text{SiSBr}_2 + 4\text{NH}_3 = \text{SiS}(\text{NH}_2)_2 + 2\text{NH}_4\text{Br}$. The precipitate is treated with liquefied NH_3 , which dissolves only the NH_4Br , operating at about 0° . The new product is a white amorphous powder, decomposed by water, uniting with HCl , &c., forming salts. The author found that well purified SiBr_4 was fusible at $+5^\circ$, and boiled at 150.8° ($h = 75.14$).—*Berichte*, vol. xxxvi., p. 4218.

MEETINGS FOR THE WEEK.

MONDAY, 23rd.—Society of Arts, 8 (Cantor Lectures). "Reservoir, Synchronic, and Fountain Pens," by James P. Maginnis, Assoc. M. Inst. C.E., &c.

TUESDAY, 24th.—Royal Institution, 5. "The Structure and Life of Animals," by Prof. L. C. Miall, D.Sc., F.R.S.
— Society of Arts, 4.30. "British Commercial Prospects in the Far East," by Byron Breckan, C.M.G.

WEDNESDAY, 25th.—Society of Arts, 8. "London Electric Railways," by Hon. Robert P. Porter.

THURSDAY, 26th.—Royal Institution, 5. "The Philosophy and Significance of 'The Tempest,'" by Prof. Burton Collins, M.A.

FRIDAY, 27th.—Royal Institution, 9. "The Life history of the Emperor Penguin," by E. A. Wilson, M.B., &c.
— Physical, 5. "Action of a Magnetic field on the Discharge through a Gas," by Dr. R. S. Wilows. "Action of Radium on the Electric Spark," by Dr. R. S. Wilows and J. Peck. "The Slow Stretch in Invarubber, Glass, and Metal Wires when Subjected to a Constant Pull," by P. Phillips. "Determination of Young's Modulus for Glass," by C. A. Bell. "Some Methods for Studying the Viscosity of Solids," by Dr. Boris Weinberg.

SATURDAY, 28th.—Royal Institution, 3. "Wat Tyler in London," by Prof. Charles Oman, M.A., &c.

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THE CHEMICAL NEWS.

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THE ATOMIC WEIGHT OF IODINE.*

By P. KÖTHNER and E. AEUER.

SHORTLY after our investigation of the atomic weight of iodine went to press, G. P. Baxter published his "Revision of the Atomic Weight of Iodine" (*Proceedings of the American Academy of Arts and Sciences*, October, 1904, vol. xl., No. 8). For the following reasons this article induced us to re-calculate the results from our experimental data, and to compare Baxter's experiences with ours.

During this examination of our results facts came to light which may perhaps be of general interest.

These deal with the question of the existence of the supposed new halogen in iodine, which Stas ("*Œuvres Complètes*," Part I., 582) was inclined to assume when the value given by him was recognised to be incorrect.

The matter stands thus:—More recent determinations all point to another value, and we are still uncertain as to the cause of this deviation.

We succeeded in proving that silver iodide as it is precipitated persistently retains a constant quantity of silver nitrate, which can only be removed by means of ammonia (*loc. cit.*, p. 30). Thus the lower value obtained by Stas may be explained in the cases in which Stas had precipitated the silver iodide from a solution of silver nitrate; but the facts that his determinations performed by means of silver sulphate and the complete analysis of silver iodide both led to the same low value, are still unexplained.

Hence we suggested that Stas's silver iodide was adulterated, not with silver nitrate but with a new halogen, of atomic weight about 62, combined with silver (*loc. cit.*, p. 47).

But, on the other hand, our own work contradicts this; for silver iodide prepared in the dry way from iodine, which had been purified by Stas's method, and which must therefore contain the new halogen, did not give Stas's value (*loc. cit.*, p. 36, *et seq.*). But if we assume with Richards that the hypothetical halogen possesses a higher atomic weight than iodine, it would be conceivable that the conditions we chose for the combination of silver and iodine led to the formation either of no stable compound of this halogen or else of no compound at all.

Baxter has now endeavoured to isolate this element of higher atomic weight than iodine (*loc. cit.*, p. 422) by preparing different fractions of iodine by repeating four times the operations of converting iodine into hydriodic acid by means of sulphuretted hydrogen, and then oxidising with potassium permanganate. With these fractions he then synthesised silver iodide in the wet way, but always arrived at the same value for iodine. Hence he concluded that iodine certainly contains no new element (*loc. cit.*, p. 428).

This argument is not conclusive; at any rate, Baxter's method of procedure could not prove anything concerning the presence of an element of lower atomic weight than iodine. Ladenburg had already noticed (*Ber.*, 1902, xxxv., [2], 1256 and 2280) that ammonia removes something from the silver iodide which has a lowering effect on the atomic weight. This fact we could confirm, and we found that ammonia is the best possible agent for purifying silver iodide, because it removes both silver chloride (and silver bromide) and silver nitrate, as well as this unknown halogen, if this should exist; for analyses of silver iodide obtained by any method whatever showed that as soon as

this iodide was treated with ammonia the higher value for iodine was invariably obtained. Now when we learn that Baxter (*loc. cit.*, p. 423) always precipitates silver iodide from strongly ammoniacal solution, and indeed with ammonium iodide, we see that he must always arrive at the same result, however different his iodine or ammonium iodide from the different fractions might be. So if we allow the possibility that an unknown halogen was contained in one of these fractions, this halogen must be kept in solution as silver haloid by the ammonia. What Baxter weighed was thus always pure silver iodide.

Thus none of his analyses can be taken as a convincing proof of the non-existence of an unknown halogen in the iodine.

In any case it is worth while examining the ammonia extracts from silver iodide. This work has already been begun by us.

Baxter, moreover, has determined the atomic weight from the proportion of silver to iodine; here also he precipitates silver iodide from an ammoniacal solution, and—as might be expected—arrives at the higher value in perfect agreement with his other syntheses.

Now we will explain the reasons which led us to calculate afresh from the experimental data all the values found by us for the atomic weight of iodine.

The third series of Baxter's determinations included analyses which were performed by Ladenburg's method, *i.e.*, the conversion of silver iodide into silver chloride; the mean value of six determinations he gave as 126.015 (126.975, O = 16). This completely confirmed the results of his other series, 126.013 (126.973) and 126.017 (126.977).

Our analyses, however, performed by Ladenburg's method led to a decidedly lower value; the mean of our nine determinations was 125.976 (126.936). But our syntheses gave 126.004 (126.964) and 126.018 (126.970), numbers which agree satisfactorily with Baxter's values.

The cause of this constant lower value obtained from the analyses seemed mysterious, for we imagined that we had taken into account all possible errors of the method and manipulation. Therefore we suggested that the relation to the atomic weight of chlorine would perhaps provide an explanation (*loc. cit.*, p. 45). This supposition has now been strikingly confirmed; for Baxter announces in his article (*loc. cit.*, p. 434) that Richards and Wells have performed a revision of the atomic weight of chlorine, which has not yet been published; they give as the atomic weight 35.199 (35.467) instead of the number hitherto accepted, 35.18 (35.45).

If this number is employed in the calculation, the mean value for iodine from our analyses comes out to 126.004 (126.964), which is identical with the result of our synthesis in the dry way.

And if in Baxter's analysis the atomic weight of iodine is referred to the old atomic weight of chlorine, a decided deviation is observed from the values calculated from those determinations which only depend upon the atomic weight of silver, and this deviation is the same as was found by us. From these facts it seems not impossible that the true proportion of silver to chlorine differs considerably from that found by Stas.

Thus our numbers agree perfectly with Baxter's, if we use for the new calculation the same constants:—Silver = 107.114 (107.930), chlorine = 35.119 (35.467).

The density of the molten silver iodide Baxter has again determined to be 5.674 (*loc. cit.*, p. 426), and the density of silver chloride was recently found by Richards and Stull to be 5.62 (*loc. cit.*, p. 434). Thus it appears that for the purpose of reduction to a vacuum, using brass weights, 0.071 m.g. must be added to each grm. of silver iodide and 0.073 m.grm. to each grm. of silver chloride.

Using these constants we obtained the following values.* (See Table I.).

* In calculating on the other basis of the atomic weights in our article we had put O = 15.88. But according to the decision of the International Atomic Weight Commission the more probable value is 15.879, which we have now used.

* Supplement to the authors' article on the same subject (*Liebig's Annalen*, 1904, cccxxxvii., 1–47).

TABLE I.

Analyses of silver iodide.	Weight of silver iodide.		Weight of silver chloride.		Proportion. AgI : AgCl.	Atomic weight of iodine.	
	In air.	In vacuo.	In air.	In vacuo.		H=1.	O=16.
1. Precipitated from neutral solution (commercial potassium iodide, pure silver nitrate); shaken for twenty-four hours with ammonia	24·87889 10·24626 12·56931 25·18689	24·88066 10·24699 12·57020 25·18868	15·18803 6·25518 7·67333 15·37566	15·18914 6·25564 7·67389 15·37678	1·6380558 1·6380362 1·6380483 1·6380983	126·002 125·999 126·001 126·008	126·962 126·960 126·961 126·968*
2. Obtained as in No. 1; evaporated with HI, shaken with NH ₃ ..	9·61938	9·62006	5·87242	5·87285	1·6380566	126·002	126·962
3. From ethyl iodide with silver solution; shaken for twenty-four hours with NH ₃	12·26683	12·26770	7·48846	7·48901	1·6380934	126·008	126·968
4. Precipitated with silver solution from hydriodic acid free from chlorine	22·60500	22·60660	13·79955	13·80056	1·6380928	126·007	126·968
5. Obtained by direct union from the elements	20·98452 22·47507	20·98601 22·47667	12·81066 13·72019	12·81160 13·72119	1·6380480 1·6380990	126·001 126·008	126·961 126·969
Mean						126·004	126·964

* We insert here these analyses, which were overlooked when we wrote our principal article.

Thus the following values are comparable :—

	H=1.	O=16.
Mean of our 9 determinations	126·004	126·964
(Error $\pm 0·005$)		
Mean of Baxter's 6 determinations..	126·015	126·975
(Error $\pm 0·005$)		
Mean of Ladenburg's 3 determinations	126·028	126·988
(Error $\pm 0·003$)		

We have calculated Ladenburg's value from his experimental data, using the new atomic weight of chlorine and the above values for the vacuum correction; the several values for O = 16 are:—126·985, 126·989, 126·991.

Baxter also re-calculated Ladenburg's number, but not directly from the analytical data; he went on the erroneous assumption that Ladenburg had taken Cl = 35·456 (O = 16) as the usual value, whereas, as a matter of fact, he took Cl = 35·45. Thus it happened that Baxter obtained a value agreeing with his, namely, 126·018 (126·978). But the values do not really agree, and the gradually increasing numbers of the above table give an interesting view of the certainty with which the analytical errors were excluded. Thus if some silver chloride escaped weighing owing to volatilisation the atomic weight would be raised to an incorrect value. Now we have experimentally proved (*loc. cit.*, p. 6) that silver chloride at the moment of formation from silver iodide is volatile to an appreciable extent, and hence we chose an apparatus by which every trace of volatilised silver chloride was included in the weighing. Our value is the lowest. Baxter also took this fact into account, and thought he had completely avoided any loss by placing a perforated porcelain plate in the Rose crucible, but even then he used a crucible which could not be completely closed. His value is somewhat higher than ours. Ladenburg carried out the transposition in a Rose crucible without the precautionary measures mentioned above, and naturally obtained the highest value.

Hence we come to the conclusion that in an atomic weight determination carried out by this method the lowest value is the most probable. The atomic weight of chlorine is perhaps accountable for the small deviation from the somewhat higher value obtained from the results of syntheses.

Finally, we were also obliged to re-calculate our syntheses so that we might be better able to compare the results.

Baxter chooses for the vacuum correction of silver

—0·031 m.grm. per grm. of silver, while we had taken —0·028 m.grm.

Synthesis in the dry way by direct union of the elements (*loc. cit.*, p. 36). 11·37576 grms. of silver gave 24·75515 grms. of silver iodide.

11·37541 grms. of silver (vac.) gave 24·75691 grms. of silver iodide (vac.). Atomic weight, 126·004 (126·964 for O = 16).

This number agrees exactly with the mean value from our analyses.

Synthesis by precipitation of hydriodic acid free from chlorine with silver solution (*loc. cit.*, p. 31).

34·51886 grms. of silver gave 75·12219 grms. of silver iodide.

34·51779 grms. of silver (vac.) gave 75·12752 grms. of silver iodide (vac.). Atomic weight, 126·018 (126·978 for O = 16).

Baxter's syntheses of silver iodide from silver showed that the atomic weight is a little higher than 126·013 (126·973); his syntheses of silver to iodine led to the value 126·017 (126·977).

These values confirm the result of our discussion in the article, that the higher value, 126·02 (126·98 for O = 16), is the most probable.

The mean of all the (41) determinations of Scott, Ladenburg, Baxter, and ourselves, if each determination is reckoned of equal value, is 126·010 (126·970 for O = 16).—*Liebig's Annalen der Chemie*, cccxxvii., p. 362).

Reduction of Manganese Oxides by Amorphous Boron, and Preparation of a New Manganese Boride.

—Binet du Jassonneix.—The protoxide, binoxide, and intermediate oxide of manganese are reduced by boron at the temperature of the blast furnace, but it is difficult to extract the metal from the mass obtained. At the higher temperature of the electric furnace the boric acid formed is volatilised, and if the heating is rapid enough a mass of non-carburated manganese-boron is formed. When the manganese oxide is in excess of the boron the melt obtained can contain 97 per cent of manganese. With, however, excess of boron the melts contain only about 20 per cent. When coarsely powdered this latter alloy burns in chlorine with incandescence, but the action stops at a certain point, and the manganese chloride is found to be mixed with a residue consisting of a definite boride of manganese, which can be isolated by washing rapidly first with water and afterwards with alcohol. An analysis of this boride shows a composition MnB.—*Comptes Rendus*, cxxxix., No. 26.

THE
EXPERT EXAMINATION OF FLUORISED WINES.

By CH. BLAREZ.

THE compounds of fluorine, such as the alkaline fluorides, fluoride of ammonium, fluoborates, and fluosilicates, have been used for a long time as antiferments, especially for rendering possible the transport and conservation of certain wines, and more particularly of those which contain non-fermented sugar, and in which the proportion of alcohol is not sufficiently high to preserve the wine, and that principally when it is inadvisable to use sulphurous acid or sulphites for fear of depreciating the wine—such is the case with red wines of which the colour is partially removed by such compounds.

Those who employ fluorides for this purpose are still, at the present time, very lucky, inasmuch as in most cases in official laboratories no search is made for the above-mentioned bodies, as the operations are long and delicate, and more often than not the methods adopted let the fluorine escape, so that the fraud is not detected.

In a paper communicated to the Société de Pharmacie de Bordeaux in the year 1886 (*Bull. Soc. Pharm. de Bordeaux*, 1886, p. 41), I announced the existence of small quantities of fluorine in natural wines; it is not necessary to argue from this fact that it is impossible for a chemist to say whether a wine has been treated with fluorised compounds or not, with the object of preserving it. In the case of natural fluorine, there are only 1 or 2 m.-grms. per litre of fluorine present. It is by the centigram, at least that we meet with it in fluorised wines.

The following is the method I adopted for the detection of traces of fluorine:—Two litres of wine were treated with a small excess of an acid solution of chloride of barium, to precipitate the whole of the sulphuric acid. After standing and filtration, the clear liquid was neutralised carefully with bicarbonate of soda. A further deposit was formed, which was collected on a filter, washed, dried, and calcined; the ashes were washed with warm water, dried, placed in a small crucible with sulphuric acid, and the crucible covered with a plate of glass partially coated with wax, leaving some portions uncovered so as to obtain etching with the hydrofluoric acid given off. The etching obtained was always very faint, and to detect it, it was often necessary to use the condensation effect of breathing on the glass with the mouth well open. These operations, as can well be seen, were very long and delicate.

Since that time I, with many others, have been called upon frequently to report on the use of fluorised compounds for the preservation of wines, and I have endeavoured to find a more convenient and rapid method for the detection of very small quantities of these compounds in wines, and one of sufficient sensitiveness that the operation could be carried out on 150 to 200 c.c. of liquid.

First of all, some years ago I examined a method of preliminary precipitation by salts of lime, a method I published in some notes intended for the students of the practical work of special analyses in the Bordeaux Faculty.

Later on, I improved this method by systematising it sufficiently to enable me to detect 0.001 grm. of fluorine in 100 c.c. of wine, which corresponds to 0.01 grm. per litre. If the result is negative we may presume the absence of fluorised compounds used as a preservative; it is better, however, to take at least 150 c.c. of wine, the results are then more definite.

The success of this test depends upon the exact carrying out of a method which must be strictly followed, and which I will now describe in detail.

We take 150 c.c. of wine, white or red, if necessary add a pinch of some alkaline sulphate. Add 10 c.c. of a 10 per cent solution of acetate of barium, shake well, and allow to settle. After a quarter of an hour, throw on to a

small folded filter of Berzelius paper. Collect the whole of the deposit on the filter. This deposit consists of sulphate of barium and some colouring materials, a small quantity of tartrate of barium, and the whole of the fluorine present in the wine, it having been transformed into fluoride of barium and deposited with the sulphate. Wash the filter once or twice, drain, and dry rapidly; it is not necessary to take any very great precautions in doing this; then incinerate in a platinum crucible with a round bottom about 5 c.m. diameter, in a gas muffle or over a Bunsen burner.

At the same time, we take a perfectly clean thin sheet of glass, round or square, 8 c.m. in diameter or width, and heat it in an oven or over a flame, and coat it over with white Carnauba wax, which, having a relatively high melting-point, is advantageous under the circumstances. After cooling, we scratch a few characters on the wax, so as to leave the glass exposed.

Cover the crucible, which should be held firmly in a support, with the plate of glass just prepared, the waxed side downwards; make sure that there is perfect contact, and heat the bottom of the crucible very moderately before covering; a small quantity of pure concentrated sulphuric acid must be added, so as to impregnate the saline matter therein.

The delicate and important point to observe, so that even traces of hydrofluoric acid may not be lost, but will etch the exposed portion of the glass, is to obtain a good and effective refrigeration of the glass plate. The method I adopted (one which can be used very generally) consists of covering the glass plate with a glass cylinder of the same diameter as the crucible, and 8 or 10 c.m. high, the lower end of which is closed with a sheet of parchment firmly attached.

This cylinder is closed at the upper end with a cork pierced with two holes allowing two tubes to pass, one going to the bottom of the cylinder and the other only just going through the cork. If we pass a continuous stream of cold water through the first tube, the cylinder becomes filled, and the excess of water escapes through the second tube, to which an indiarubber tube is attached to carry the water off. The pressure of water presses the parchment closely to the glass plate, which is in this manner kept continuously cold.

After an hour the heat is withdrawn, the plate detached, and the wax removed by heating it and cleaning it, first with paper, then with either powdered cether or precipitated chalk and a little chloroform or tetrachloride of carbon. The clean plate is then examined. When the wine has been fluorised by the addition of an antiseptic fluorine compound the etching is sharp, and can be seen with the naked eye, and by means of a lens or the microscope and a pointed needle we can observe that the glass has been actually eaten into.

I may say, in concluding, that in most cases fluorine compounds are used as antiseptics in such doses that 4 or 5 centigrams. per litre can be found, corresponding to about 8 or 10 grms. of fluoride of sodium or of ammonium per hectolitre.

With wines containing non-fermented sugar the dose present may be double this quantity. But often the amount found is lower, either because it has been added at such a time that the wine has been kept for a long while either in bottles or casks before being analysed. The fluorine is then deposited to a certain extent in an insoluble form in the lees, in which it is easily found.

I would also remark that, with the object of rendering their detection more difficult, the fluorides are combined with neutral sulphates. Alkaline benzoates are also added. It follows that the detection of these compounds, each of which is present in very small quantities only, is a very difficult operation.

The method I have described enables us in every case to detect fluorine in a wine when any of its compounds has been introduced as an antiseptic or an antiferment.—*Bull. des Trav. de la Soc. de Pharm. de Bordeaux*, 1904, p. 321.

THE ACTION OF HYDROGEN PEROXIDE
UPON ANHYDRIDES,
AND THE FORMATION OF ORGANIC ACID,
PEROXIDES, AND PERACIDS.*

By A. M. CLOVER and A. C. HOUGHTON.

(Concluded from p. 32).

Anhydrides of Dibasic Acids (continued).

Succinic Monoperacid, $\begin{array}{c} \text{CH}_2\text{COOH} \\ | \\ \text{CH}_2\text{COOOH} \end{array}$ —Ten grms. of succinic peroxide acid were covered with about 75 c.c. water in a beaker and stirred continuously at a temperature of about 30°. At the end of three or four hours the entire amount had gone into solution. It was then removed to an evaporating-dish and allowed to remain in a vacuum over night with sulphuric acid. The dry residue consisted of about 45 per cent of succinic monoperacid. The monoperacid is more soluble in chloroform than succinic acid, and may be removed from the latter by digesting the mixture with chloroform at 50°, filtering, and cooling the solution. In this way the substance is obtained fairly pure. It may be re-crystallised from a mixture of chloroform and ether, from which it separates in large crystals on standing. The percentage of active oxygen contained by various samples which were re-crystallised several times varied from 10.5 to 11.3, while the theoretical is 11.9. This deficiency may have been due to the fact that when the substance is dissolved in water a decided evolution of oxygen is noticeable; it was necessary to dissolve in water to estimate the active oxygen. A sample re-crystallised twice contained 11 per cent of active oxygen, and when rapidly heated melted at 107° with decomposition.

0.1170 grm. substance gave 0.1546 grm. CO₂ and 0.0473 grm. H₂O.

	Calculated for C ₄ H ₆ O ₅	Found.
C	35.81	36.03
H	4.52	4.53

The substance is much more soluble in water than succinic acid. The same relation exists between the solubilities of benzoic acid and peracid. It also dissolves freely in alcohol, acetone, and acetic ether. It is only moderately soluble in ether, and sparingly in chloroform. It has very little, if any, odour, and does not in the least remind one of hypochlorous acid, as do benzoic and acetic peracids. It gradually decomposes on standing, but is more stable than benzoic peracid. A sample consisting of a mixture of succinic acid and monoperacid was found on analysis to consist of 60 per cent of the latter. After standing for a week in a stoppered vessel the percentage of monoperacid was only 55.4.

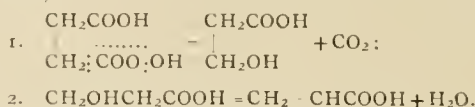
When a strong aqueous solution of the substance (either pure or mixed with succinic acid) is saturated with succinic anhydride, a heavy precipitate of succinic peroxide acid soon appears; more quickly on cooling and scratching with a glass rod. When glutaric anhydride is dissolved in a strong solution of the monoperacid, the mixed peroxide acid of succinic and glutaric acids is formed, and on cooling separates from the solution. This substance will be described later.

The decomposition of succinic monoperacid is interesting. The mixture of acid and monoperacid was used for this study. It was mixed with infusorial earth in order to moderate the action.

Three and five-tenths grms. of the mixed acids containing 1.6 grms. of monoperacid were mixed with 5 grms. of infusorial earth and placed in a small flask connected with a carbon dioxide generator and a gasometer. The

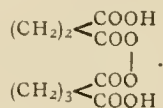
air in the flask was completely replaced by carbon dioxide and the flask was then slowly heated in an oil-bath, and the gas evolved was collected over water in the gasometer. The volume of gas evolved was about 350 c.c. This consisted almost entirely of carbon dioxide, with only a trace of oxygen and a small amount (about 3 per cent) of a combustible gas. The amount of carbon dioxide obtained is a little in excess of 1 molecule from 1 molecule of the monoperacid.

The experiment was repeated in order to determine the nature of the non-gaseous products. After the decomposition was completed, the contents of the flask were distilled. Considerable water passed over at first, and the temperature gradually rose to 140°. The distillate possessed the characteristic odour of acrylic acid. That it consisted in a large part of this substance was shown by treating it with concentrated hydriodic acid, whereupon β-iodopropionic acid crystallised from the solution. This was re-crystallised from water and identified by its melting-point. The decomposition may be explained as follows:—



The substance first splits off carbon dioxide. The β-hydroxypropionic acid, which is probably formed as an intermediate product, then splits off water with the formation of acrylic acid. The decomposition probably takes place almost entirely in the manner indicated. Baeyer found that benzoic peracid decomposed with the formation of benzoic acid and oxygen. The results obtained with succinic monoperacid have suggested that possibly phenol is also formed during the decomposition of benzoic peracid. This is made probable from the fact that benzoic peracid becomes coloured on standing. Phthalic monoperacid, discovered and described by Baeyer, was found to yield salicylic acid on decomposition. This was identified by its colour test with ferric chloride.

Succinic Glutaric Peroxide Acid,—



—Ten c.c. of a solution of succinic monoperacid containing 1.47 grms. of this substance, and which was free from hydrogen peroxide, was treated with 1.5 grms. of glutaric anhydride. The latter substance was dissolved after shaking for a minute. The solution was kept cool under a tap, and after about five minutes a crystalline precipitate appeared. After standing for five minutes longer the product was filtered, washed several times with small portions of water, and packed tightly on a porous plate. When dry, the substance was practically pure. Yield, 1.2 grms. For analysis it was re-crystallised from a mixture of ether and acetic ether.

0.0825 grm. substance required 13.25 c.c. N 20 thio-sulphate.

0.1473 grm. substance gave 0.2344 grm. CO₂, and 0.0650 grm. H₂O.

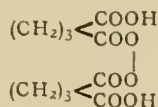
	Calculated for C ₉ H ₁₂ O ₈	Found.
C	43.52	43.40
H	4.88	4.96
O (active)	6.45	6.40

The substance begins to soften at 105° and melts at 107° with decomposition. It is quite soluble in alcohol, acetone, and acetic ether, and sparingly soluble in ether. The crystals are similar in appearance to those of succinic peroxide acid. When potassium iodide is added to a

* From the *American Chemical Journal*, xxxii., No. 1.

saturated solution of the substance, it must stand two or three minutes before the theoretical amount of iodine is liberated. In oxidising action it is, therefore, less powerful than succinic peroxide acid.

Glutaric Peroxide Acid,—



—Three grms. of glutaric anhydride were dissolved in 6 c.c. of 8 per cent hydrogen peroxide. The solution was kept cool, and the peroxide acid soon crystallised out. After twelve minutes it was filtered off, washed well with small portions of water, and dried on a porous plate. The dried substance was practically pure. Yield, 1.9 grms. For analysis it was crystallised from acetic ether.

0.0888 gm. substance required 13.25 c.c. N 20 thio-sulphate.

0.1578 gm. substance gave 0.2640 gm. CO₂ and 0.0756 gm. H₂O.

	Calculated for C ₁₀ H ₁₄ O ₈ .	Found.
C	45.77	45.61
H	5.39	5.37
O (active).. .. .	6.10	5.97

The substance melts sharply at 108° with decomposition. It is quite soluble in alcohol, acetone, and acetic ether; moderately soluble in ether; and very sparingly in chloroform and benzene. The substance hydrolyses in aqueous solution, and the solubility and rate of hydrolysis were determined at 24° in the same manner as with succinic peroxide acid.

The amounts of peroxide acid contained in 1 litre of solution at intervals of five, ten, fifteen, and twenty-five minutes were 9.75, 10.75, 11.6, and 13.75 grms. respectively. At this rate of hydrolysis the original solubility may be placed approximately at 8.75 grms. per litre.

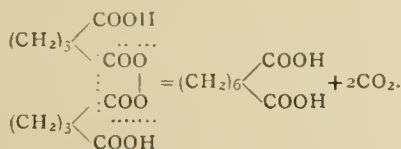
The action of glutaric peroxide acid upon potassium iodide is markedly different from that of succinic peroxide acid. The action is very slow, like that of hydrogen peroxide. As in the case of the latter substance, the time required for the complete liberation of iodine is greatly decreased by the addition of dilute sulphuric acid. Except in very dilute solution of peroxide, the theoretical amount of iodine is liberated in fifteen minutes when excess of potassium iodide has been added.

The decomposition of glutaric peroxide acid was studied in the same manner as that of the succinic compound.

Four and five-tenths grms. of the substance were added in small portions to 15 c.c. of boiling xylene. The non-volatile products of decomposition remain dissolved, but, on cooling, 0.6 gm. of colourless crystals was deposited. This product was found to be almost pure suberic acid. The substance was purified by re-crystallising from water, and melted at 140° (suberic acid 140°).

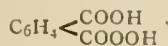
0.1156 gm. substance required 13.45 N/10 KOH.
Calculated, 13.3 c.c.

On distilling off the xylene from the filtrate previously mentioned, a fatty residue remained which was soluble in sodium carbonate. The decomposition takes place only to a certain extent as follows:—

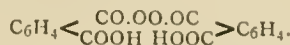


By the action of sodium hydroxide and hydrogen peroxide

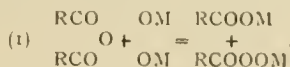
upon phthalic anhydride, Baeyer and Villiger (*Ber.*, xxxiv., 762) have isolated phthalic monoperacid,—



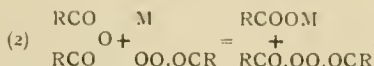
and phthalic peroxide acid,—



These authors have offered no explanation of the reactions involved. If we consider that the addition of an alkali to a solution of hydrogen peroxide results in the formation of a salt of this substance, either MOOH or MOOM, then the reaction between such a solution and an anhydride may be looked upon as follows:—



and—



Such a view would explain all of the reactions which are known to take place between sodium peroxide, barium peroxide, &c., and acid anhydrides, chlorides, &c. This explanation is, however, not in accord with the views of Calvert (*Zeit. Phys. Chem.*, xxxviii., 513), who, after attacking from all sides the problem of the condition of hydrogen peroxide in alkaline solution, arrived at the conclusion that a compound of the type MO₂ is formed, M being a univalent metal. The work of Calvert has certainly shown that 1 molecule of alkali is capable of holding in combination more than 1 molecule of hydrogen peroxide. This behaviour might be due to the formation of an addition-compound between hydrogen peroxide and its primary salt, such as KHO₂.H₂O. Schöne has isolated compounds of this type by evaporating an alkaline solution of hydrogen peroxide in a vacuum (*Liebig's Ann. Chem.*, xcxciii., 241). A compound containing sodium acetate and hydrogen peroxide crystallises out on adding sodium peroxide to acetic acid (*Tafel, Ber.*, xxvii., 816). Tanatar has isolated compounds between other salts and hydrogen peroxide (*Zeit. Anorg. Chem.*, xxviii., 255). Calvert showed that the solubility of potassium chlorate is greater in a solution of hydrogen peroxide than in water, and that its electric conductivity is less, although it would be expected to be greater, on account of the dielectric constant of hydrogen peroxide being greater than that of water. Jones and Carroll (*Am. Chem. Journ.*, xxviii., 284) further found that the depression of the freezing-point, brought about by various salts in hydrogen peroxide solution, was less than that in water, and have pointed out the probability that compounds are formed between hydrogen peroxide and salts in solution. An unstable compound between the benzoylated hydrogen peroxide and its sodium salt has been observed by Baeyer and Villiger (*Ber.*, xxxiii., 1569). A number of weak acids are known to form compounds of this type, and we may even look at compounds containing water of crystallisation in the same light. It is not known whether or not such compounds are completely dissociated in aqueous solution. The similarity between hydrogen peroxide and water which has been pointed out in this article makes it appear possible that water enters into combination with neutral salts dissolved in it. In this connection the results obtained by Calvert and by Jones and Carroll appear especially interesting.

The following may be summed up as the chief reactions which are known to take place when an anhydride is dissolved in an aqueous solution of hydrogen peroxide:—

1. Ordinary hydrolysis with water.
2. Analogous reaction with hydrogen peroxide resulting in the formation of a peracid.
3. Action of peracid on anhydride with the formation of an acid peroxide.

4. Ordinary hydrolysis of peroxide with water.
5. Action of hydrogen peroxide upon acid peroxide with the formation of 2 molecules of peracid and also with loss of oxygen, possibly due to the intermediary formation of a derivative of hydrogen trioxide.

6. Slow hydrolysis of peracid to acid and hydrogen peroxide.

7. Slow decomposition of both peracid and hydrogen peroxide with evolution of oxygen.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING DECEMBER 31ST, 1904.

By SIR WILLIAM CROOKES, F.R.S.,

and
SIR JAMES DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, January 12th, 1905.

SIR,—We submit herewith, at the request of the Metropolitan Water Board, the results of our analyses of the 204 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the Metropolitan Water Board taking their supplies from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Dec. 1st to Dec. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 204 samples examined by us during the month, all were clear, bright, and well filtered.

Again, the rainfall at Oxford has been below the average. The actual amount of rain measured during December was 1.86 inches; the average for the month is 2.16 inches; thus we have a deficit of 0.30 inch, which, if added to the previous deficit of 2.32 inches, gives a total deficit for the year of 2.62 inches, which is 10.3 per cent below the thirty-five years' average.

TABLE A.—Rainfall in Inches at Oxford, Month by Month, during the Year 1904.

	Actual fall. Inches.	Mean of 35 years. Inches.	Difference from the mean	
			Inches.	Inches.
January ..	3.10	2.08	—	+1.02
February ..	2.98	1.80	—	+1.18
March ..	1.05	1.47	-0.42	—
April ..	0.81	1.61	-0.80	—
May ..	3.20	1.75	—	+1.45
June ..	1.04	2.10	-1.06	—
July ..	3.35	2.49	—	+0.86
August ..	1.61	2.38	-0.77	—
September..	1.26	2.39	-1.13	—
October ..	0.82	2.76	-1.94	—
November ..	1.59	2.30	-0.71	—
December ..	1.86	2.16	-0.30	—
	22.67	25.29	-7.13	+4.51

Our bacteriological examinations of 377 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 384 others from special wells, standpipes, &c., making 761 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	357
New River, filtered (mean of 71 samples) ..	12
Thames, unfiltered (mean of 26 samples) ..	5875
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 203 samples) ..	29
Ditto ditto highest	310
Ditto ditto lowest	0
River Lea, unfiltered (mean of 26 samples) ..	331
River Lea, from the East London District clear- water wells (mean of 25 samples) ..	30

Of the 299 daily samples taken from the general filter wells of the Metropolitan Water Board, thirteen samples, or 4.3 per cent, were sterile. Twenty-four samples, or 8.0 per cent, contained more than 100 microbes, and of these four samples contained more than 150 microbes per c.c. The twenty-four excess samples contained an average of 134 microbes per c.c. In November eight samples contained an average of 140 microbes per c.c.

The above figures show that though the actual numbers of microbes in the filtered water was a little higher than in the previous month, the ratio of efficiency of filtration was much better.

TABLE B.—Showing the Average Monthly Bacterial Variations during the Year 1904.

Month.	Thames, unfiltered.	Thames- derived supplies, filtered.	New River, unfiltered.	New River, filtered.	River Lea, unfiltered	River Lea (East London District), filtered.	
January ..	8797	21	310	16	341	14	
February ..	19530	39	848	33	347	27	
March ..	7410	17	210	11	187	9	
April ..	4798	19	109	15	150	7	
May ..	4120	15	116	4	225	19	
June ..	883	20	112	6	182	12	
	7589	21	284	14	238	14	Mean of 1st 6 months.
July ..	7589	17	1572	8	567	11	
August ..	988	22	142	5	231	7	
September ..	801	17	138	5	250	7	
October ..	2449	11	217	8	271	14	
November ..	2407	13	200	8	236	16	
December ..	5875	29	357	12	331	30	
	3351	19	437	7	314	14	Mean of 2nd 6 months.
	5470	20	360	10	276	14	Mean of 12 months.

TABLE C.—Average Number of Microbes in the Filtered London Waters for the Past Eight Years.

	Thames-derived supplies.	New River.	River Lea
1897	46	32	62
1898	34	30	25
1899	27	15	20
1900	21	9	10
1901	24	10	22
1902	27	13	25
1903	36	16	26
1904	20	10	11

TABLE D.—Averages of the Supplies derived from the River Thames during the Year 1904

	Common salt per gallon.	Nitric acid per gallon.	Hardness. Degrees.	Oxygen required per gallon.	Organic carbon per gallon.	Organic carbon per gallon.	Colour. Brown: Blue
	Means.	Means.	Means.	Means.	Means.	Maxima.	Means.
January	2 009	1'326	17 44	0'043	0'153	0'210	14'6 : 20
February	1 927	0'994	15'81	0'065	0'202	0'269	21 8 : 20
March	1 888	1 147	16 59	0'040	0'142	0 216	12 4 : 20
April	1'937	1'011	15'16	0'033	0'099	0'125	10 0 : 20
May	1 968	0'987	14'40	0'031	0'089	0'129	10 7 : 20
June	2'001	0 841	14 53	0'049	0'122	0 205	19 2 : 20
July	2'020	0'851	13'45	0'035	0'083	0 116	15'8 : 20
August	2'017	0'807	13'26	0'035	0'032	0 125	16'8 : 20
September .. .	2'107	0'810	13 43	0'027	0'074	0 092	16'2 : 20
October	2'160	1'031	13'85	0'026	0'075	0 092	15 3 : 20
November .. .	2'184	1'001	14 63	0'028	0 097	0 131	17 8 : 20
December .. .	2'290	1'036	15'12	0'040	0 142	0 219	19 6 : 20

During the past year we have examined 9146 samples of London waters bacteriologically, as compared with 8022, 6953, 6893, and 6731 respectively in the four previous years. We have also made 2631 chemical analyses of London waters throughout this period, making a total of 11,777 samples examined during the year.

Table B gives the bacteriological results for the past year. During the first six months the Thames-derived Districts' clear-water wells contained on an average 21 bacteria per c.c., while the New River and River Lea supplies each contained 14. During the second six months the numbers of bacteria in the waters from the same three sources were 19, 7, and 14 respectively.

Table D gives the average chemical composition of the Thames-derived supplies during the year 1904. It will be observed that the amount of organic carbon present has been remarkably low during the autumn; this is no doubt due to the low rainfall, and may be expected to increase during the coming winter and spring.

The average microbic impurity of the Thames-derived supply during the year 1904 has been much less than it was in 1903, and the same remark applies to the supplies from the new River and the River Lea.

Taken as a whole, the purification of the London water by the combined action of storage and filtration during the past year has been highly satisfactory.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

Royal Institution.—On Thursday next, February 2, at 5 o'clock, Prof. W. Schlich delivers the first of a course of two lectures at the Royal Institution on "Forestry in the British Empire"; and on Saturday, February 4, at 3 o'clock, Sir Alexander Mackenzie begins a course of three lectures on "The Bohemian School of Music" (with Musical Illustrations). The Discourse on Friday, February 3, will be delivered by Prof. T. Clifford Allbutt on "Blood Pressure in Man," and on Friday, February 10, by Dr. Cecil Smith on "The Art of the Ionian Greeks."

REPORT OF THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS.*

THE International Committee on Atomic Weights respectfully submits the following report, together with a table of atomic weights for use during 1905.

Most of the values recommended in our table are identical with those reported in former years, but a few changes seem to be needed. Other changes, which are suggested by recent investigations, are deferred until fuller information regarding their desirability shall have been received. During 1904 there has been great activity in the determination of atomic weights; and a summary of the more important researches may help to explain our reasons for changing or retaining hitherto accepted values. The researches to be considered are as follows:—

Glucium.—The atomic weight has been re-determined by Parsons (*Journ. Am. Chem. Soc.*, xxvi., 721). Seven analyses of the acetylacetate gave, in mean, $\text{Gl} = 9.113$. Nine analyses of the basic acetate gave exactly the same average. As the individual determinations range from 9.081 to 9.142, the figure 9.1 may evidently remain unchanged.

Indium.—The investigation by Thiel shows that the atomic weight of indium is higher than had been supposed (*Zeit. Anorg. Chem.*, xl., 280). Analyses of the trichloride gave, in mean, $\text{In} = 115.05$. Analyses of the tribromide gave 114.81. With the oxide, unsatisfactory results were obtained. For present purposes the round number 115 may be adopted, although further investigation is promised by Thiel, and a research by Dennis and Geer is in progress.

Iodine.—In our former reports we have noted the uncertainty in the accepted atomic weight of iodine. Stas, by the synthesis of AgI , found $\text{I} = 126.85$. Scott, by the same general method, found $\text{I} = 126.97$, and Ladenburg, by measuring the ratio $\text{AgI}:\text{AgCl}$, obtained the value 126.96. Koethner and Auer (*Ber.*, xxvii., 2536), from data given by several methods, including a repetition of Ladenburg's process, conclude that the atomic weight of iodine cannot be less than 126.963, but the full details of their investigation, at the date of writing this report, are

* *Journal of the American Chemical Society*, xxvii., No. 1.

unpublished. A more recent research by G. P. Baxter will soon appear,* in which the higher value for iodine is completely confirmed, both by Ladenburg's method and by that of Stas. Baxter's final value is 126.975 , and there can now be no reasonable doubt that the Stas figure is too low. The number 126.97 is adopted in our table for $O = 16$, or 126.01 with hydrogen as unity.

Nitrogen.—The accepted value for the atomic weight of nitrogen, 14.04 , is derived mainly from the work of Stas. Of late years, however, the study of gaseous densities has led several physicists, notably Rayleigh, Leduc, and Daniel Berthelot, to the belief that the true value is but little in excess of the round number 14 . Guye finds, from the density of nitrogen, the value 14.004 (*Comptes Rendus*, cxxxviii., 1213). Still more recently, Guye and Bogdan, by analysis of nitrous oxide, have found $N = 14.007$ (*Comptes Rendus*, cxxxviii., 1494). Jaquero and Bogdan have also studied nitrous oxide volumetrically, and obtained the figure 14.019 (*Comptes Rendus*, cxxxix., 49). In view of the discordance between the volumetric and the gravimetric data, it seems undesirable to make any change at present in the number assigned to nitrogen. Further investigation of this atomic weight is evidently needed.

Rubidium.—Atomic weight re-determined by Archibald from analyses of the chloride and bromide (*Journ. Chem. Soc.*, lxxxv., 776). The final mean, derived from many concordant experiments, is $Rb = 85.485$. As some of the determinations are slightly higher than 85.5 , that figure may be adopted as sufficiently accurate for all practical purposes.

Samarium.—Urbain and Lacombe, by analyses of the octohydrated sulphate, find $Sm = 150.34$ (*Comptes Rendus*, cxxxviii., 1166). A comparison of this figure with the older determinations justifies the use of 150.3 as the most probable value for this atomic weight. The same authors have also determined the atomic weight of europium, and give the figure $Eu = 151.79$ (*Comptes Rendus*, cxxxviii., 627). It is desirable, however, to await more complete information about europium before recognising it in the table.

Thorium.—Evidence as to the complex nature of ordinary "thorium" is steadily accumulating. According to Baskerville it is a mixture of at least three elements, which he calls carolinium, thorium, and berzelium (*Journ. Am. Chem. Soc.*, xxvi., 922). Their approximate atomic weights are 256 , 220 , and 212.5 respectively, supposing them all to be tetrads. The value in our table is that of ordinary thorium, as it is found in mineral analyses, and no change can safely be made until our knowledge has become more definite.

Tungsten.—The figure commonly assigned to tungsten, $W = 184$, has been verified by Smith and Exner (*Proc. Am. Phil. Soc.*, xliii., 123; *Journ. Am. Chem. Soc.*, xxvi., 1082). From 27 measurements of the ratio $WCl_6:WO_3$, $W = 184.04$. From 23 syntheses of WO_3 , $W = 184.065$. The individual determinations range from 183.94 to 184.14 , which is a fair degree of concordance for so high an atomic weight.

Changes, then, are recommended in the cases of indium, iodine, rubidium, and samarium. The column of atomic weights which referred to the hydrogen unit has also been carefully re-calculated, and in it some small alterations appear. The latter modifications, however, are unimportant, except in so far as they help to bring the two tables into greater harmony.

During the year there has been a revival of the agitation over the question of standards, and the policy of this committee, or rather sub-committee of the larger international body, in publishing a double table, has encountered some criticism. That criticism is perfectly legitimate, and we are glad to say that it has been expressed courteously, and in a truly scientific spirit. Professors Sakura and Ikeda

(*CHEMICAL NEWS*, lxxxix., 305) have published an open letter upon the subject,* and in response to a demand within the German Chemical Society, the committee representing that body issued a circular to the members of the larger International Committee, asking for an expression of opinion as to our procedure. We are not yet informed regarding the responses to that circular, and we therefore cannot base any action upon it. The Council of the American Chemical Society has also, by a formal vote, requested this committee to ask for instructions from the larger body, both as to the use of a double standard, and as to the nomenclature and symbols of glucinum or beryllium, and columbium or niobium. With this request we now comply, and hope that every member of the larger International Committee on Atomic Weights will send us his opinion upon the questions thus raised. Shall we continue to issue a double table? Can uniformity in symbols and nomenclature be obtained? And which names are preferable, in the light of history, evidence, and international usage, for the two elements under discussion?

That a single standard for atomic weights is most desirable, every chemist will admit; but two standards actually exist, and each one is represented by earnest advocates who are unwilling to give way. Each side of the controversy is supported by eminent authorities in nearly equal numbers, and no agreement seems to be possible either at present or within the near future. This condition of affairs the present committee has been compelled to face, and to deal with things as they are instead of as we should like them to be. Two tables of atomic weight are current, and it has therefore seemed wisest to recognise the needs of both parties in the controversy, and to furnish each with trustworthy data for practical use. It is surely better to have one committee prepare both tables, than to leave this work to be done in accordance with individual preferences. That there are difficulties in adjusting one table to the other is perfectly evident, but the resulting confusion is, we think, less serious than some of our critics would have us believe. The confusion is certainly less than it would be, were the individual advocates of either standard to attempt the adjustment of one to the other independently. In short, the real question now before us seems to be this:—Shall the present committee act in a quasi-judicial manner, recognising both parties in controversy, or shall it assume a partisan position and represent one alone?

(Signed).

F. W. CLARKE,
T. E. THORPE,
KARL SEUBERT,
HENRI MOISSAN, } Committee.

International Atomic Weights.

		O = 16.	H = 1
Aluminium	Al	27.1	26.9
Antimony	Sb	120.2	119.3
Argon	A	39.9	39.6
Arsenic	As	75.1	74.4
Barium	Ba	137.4	136.4
Bismuth	Bi	208.5	206.9
Boron	B	11.0	10.9
Bromine	Br	79.96	79.36
Cadmium	Cd	112.4	111.6
Cæsium	Cs	132.9	131.9
Calcium	Ca	40.1	39.7
Carbon	C	12.00	11.91
Cerium	Ce	140.25	139.2
Chlorine	Cl	35.45	35.18
Chromium	Cr	52.1	51.7
Cobalt	Co	59.0	58.55
Columbium	Cb	94	93.3
Copper	Cu	63.6	63.1
Erbium	Er	166	164.8

* Since writing the above, the paper referred to has been published (*Journ. Am. Chem. Soc.*, xxvi., 1577).

* See reply by F. W. Clarke in *CHEMICAL NEWS*, xc., 56, July 29, 1904.

		O=16.	H=1.
Fluorine	F	19	18'9
Gadolinium	Gd	156	154'8
Gallium	Ga	70	69'5
Germanium	Ge	72'5	72
Glucinum	Gl	9'1	9'03
Gold	Au	197'2	195'7
Helium	He	4	4
Hydrogen	H	1'008	1'000
Indium	In	115	114'1
Iodine	I	126'97	126'01
Iridium	Ir	193'0	191'5
Iron	Fe	55'9	55'5
Krypton	Kr	81'8	81'2
Lanthanum	La	138'9	137'9
Lead	Pb	206'9	205'35
Lithium	Li	7'03	6'98
Magnesium	Mg	24'36	24'18
Manganese	Mn	55'0	54'6
Mercury	Hg	200'0	198'5
Molybdenum	Mo	96'0	95'3
Neodymium	Nd	143'6	142'5
Neon	Ne	20	19'9
Nickel	Ni	58'7	58'3
Nitrogen	N	14'04	13'93
Osmium	Os	191	189'6
Oxygen	O	16'00	15'88
Palladium	Pd	106'5	105'7
Phosphorus	P	31'0	30'77
Platinum	Pt	194'8	193'3
Potassium	K	39'15	38'85
Praseodymium	Pr	140'5	139'4
Radium	Ra	225	223'3
Rhodium	Rh	103'0	102'2
Rubidium	Rb	85'5	84'9
Ruthenium	Ru	101'7	100'9
Samarium	Sm	150'3	149'2
Scandium	Sc	44'1	43'8
Selenium	Se	79'2	78'6
Silicon	Si	28'4	28'2
Silver	Ag	107'93	107'11
Sodium	Na	23'05	22'88
Strontium	Sr	87'6	86'94
Sulphur	S	32'06	31'82
Tantalum	Ta	183	181'6
Tellurium	Te	127'6	126'6
Terbium	Tb	160	158'8
Thallium	Tl	204'1	202'6
Thorium	Th	232'5	230'8
Thulium	Tm	171	169'7
Tin	Sn	119'0	118'1
Titanium	Ti	48'1	47'7
Tungsten	W	184	182'6
Uranium	U	238'5	236'7
Vanadium	V	51'2	50'8
Xenon	Xe	128	127
Ytterbium	Yb	173'0	171'7
Yttrium	Yt	89'0	88'3
Zinc	Zn	65'4	64'9
Zirconium	Zr	90'6	89'9

Copies of the report as drawn and agreed to were sent to England, France, Germany, Italy, and Japan for simultaneous publication. It is therefore, in the opinion of Professors Thorpe, Seubert, and myself, too late to attempt any change for the current year. To withdraw, re-write, and re-sign the report would involve too great a delay. We therefore ask for patience on the part of the larger committee, whose wishes will receive due consideration next year.

F. W. CLARKE.

KUNZITE AND ITS UNIQUE PROPERTIES.

By CHARLES BASKERVILLE and GEORGE F. KUNZ.

IN a recent investigation (*Science*, N.S., 1903, xviii., 769) made by us on the behaviour of a large number of minerals and gems with various forms of radiant energy, including the emanations, as well as on the production of luminescence in some cases by other physical means, the new variety of spodumene, designated kunzite, was found to be peculiarly sensitive, and to exhibit some remarkable properties.

In general, as shown by these investigations, the gem-minerals were little affected by ultra-violet rays; but three species exhibited a high degree of responsiveness to these and to all forms of radio-activity, so far experimented with. These minerals were diamonds of certain kinds, willemite (zinc orthosilicate), which in some cases has been used as a gem-stone, and kunzite. The behaviour of the last, as noted in various experiments, is unique, and will be briefly described here by itself.

1. *Attrition and Heat.*—Kunzite does not become luminous by attrition or rubbing. Several specimens were held on a revolving buff cloth making 3000 revolutions per minute, so hot as to be almost unbearable to the hand, and still it failed to become luminous. Wollastonite, willemite, and pectolite are, however, very tribo-luminescent.

As to luminescence induced by heat alone, it was found that kunzite does possess the property of thermo-luminescence to some extent, with an orange tint and at a low degree of heat.

2. *Electricity.*—The mineral assumes a static charge of electricity, like topaz, when rubbed with a woollen cloth. On exposing kunzite crystals of different sizes to the passage of an oscillating current obtained from large Helmholtz machines, the entire crystal glowed an orange-pink, temporarily losing the lilac colour. A well-defined brilliant line of light appeared through the centre, apparently in the path of the current. On discontinuing the current, the crystal gave the appearance of a glowing coal. It was not hot, however, and the phosphorescence lasted for forty-five minutes.

Three large crystals, weighing 200, 300, and 400 grms. each, were attached to copper wires so that the current passed in one instance from below up, and from the other upwards across the crystal—first across the prism, then parallel with the prism. In each instance the crystals became distinctively luminous, a pale orange-pink, and between the two wires a bright almost transparent line passed from one wire to the other; in reality, as if the two elongated cones crossed each other, the line of the path being transparent at the sides, whereas the rest of the crystals appeared translucent. After the exposure of two minutes, they were laid upon photographic plates, and in five minutes produced a fine auto-print. The crystals continued to glow for forty-five minutes.

When a cut gem is suspended between the two poles, it becomes an intense orange-pink colour, glowing with wonderful brilliancy. The discharge seemed as if it would tear the gem asunder, although actually it was unaffected.

3. *Ultra-violet Rays.*—These invisible rays, produced by sparking a high voltage current between iron terminals,

Addendum.—Since the foregoing report was written, signed, and sent in for publication, the vote of the larger committee, as solicited by the Committee of the German Chemical Society, has been received. Fifty-nine members of the larger committee are therein recognised. Thirty-one voted for a table based upon O = 16 exclusively; two for H = 1 exclusively; and five for the simultaneous use of both standards. To the last vote should be added that of the four members of the smaller committee, making nine in all for the double table. Seventeen members refrained from voting. The vote, then, gives one more than a majority of the entire committee in favour of the oxygen standard alone, although the committee appointed by the Chemical Society of Paris in 1900 seems not to have been consulted.

caused kunzite, white, pink, or lilac, to phosphoresce for some minutes. The white responded most readily.

4. *Röntgen, or X-Rays.*—All forms of kunzite become strongly phosphorescent under these rays. An exposure of half a minute caused three cut gems to glow first a golden-pink, and then white for ten minutes. The glow was visible through two thicknesses of white paper, which was held over it. A large crystal excited for five minutes afterwards effected a sensitive photographic plate (*Science*, N.S., 1903, xviii., 303). Another crystal, exposed for ten minutes, was laid for five minutes on a sensitive plate. (This was made by Dr. H. G. Piffard, of New York City). The resulting auto-photograph was clear and distinct, but presented a very curious aspect not seen by the eye—as of a misty or feathery outflow from the side and termination of the crystal, suggesting an actual picture of the invisible lines of force. The other varieties of spodumene, mineral material, and cut gems, failed to show this property. We are not yet in a position to offer a satisfactory explanation of the above.

Whereas kunzite is so responsive and fluorescent, and so beautiful upon exposure to the X-rays, it is, however, like all silicates, opaque to the ray itself. Four crystals weighing 100, 200, and 400 grms. each, were exposed to the Röntgen ray for two minutes. They became first a beautiful rose-orange, then assumed a white phosphorescence, and at the end or forty-five minutes there was still a faint residual glow. Two minutes exposure to the X-ray caused them to print a perfect auto-type. The glow in all instances showed first a rose-orange colour, then a pale pink, finally resolving into a white fluorescence; the auto-print shows the feathery outlines of light or energy thrown out by the crystal.

5. *Conduct with Radium Preparations.*—Exposed for a few minutes to radium bromide with a radio-active strength of 300,000 (uranium being taken as unity), the mineral becomes wonderfully phosphorescent, the glow continuing persistently after the removal of the source of excitation. The bromide was confined in glass. Six hundred grms. of kunzite crystals were thus excited with 127 m.grms. of the radium bromide in five minutes. The effect is not produced instantaneously, but is cumulative, and after a few moments exposure the mineral begins to glow, and its phosphorescence is pronounced after the removal of the radio-active body. The luminosity continued in the dark for some little time after the radium was taken away. No other varieties of spodumene examined, including hiddenite, gave like results. In this respect, as with the Röntgen rays, the kunzite variety stands by itself.

When pulverised kunzite is mixed with radium-barium chloride of 240 activity, or carbonate of lower activity, the mixed powder becomes luminous and apparently remains so permanently, i.e., in several months no loss has been observed. The same is the case if pulverised wollastonite or pectolite be used instead of the kunzite. When either of these mixtures is put in a Bologna flask and laid on a heated metal plate (less than red-hot), the powder becomes incandescent and remains so for a long time after removal.

These three minerals phosphoresce by heat alone, as was mentioned above in regard to kunzite. Perhaps this luminosity of the mixed powders at the ordinary temperature may be accounted for in part by the evolution of heat on the part of the radium compounds (P. Curie and Laborde, *Comptes Rendus*, cxxvii., 673), but there are experimental reasons which cause us to reject such explanation for the total effect.

The emanation of radium, the α -rays, according to Rutherford (*Phil. Mag.*, v., 561), are condensed at a temperature of -130 to -140° C. The emanations were driven from radium chloride by heat and condensed with liquid air on a number of kunzite crystals, according to a method which will be described by one of us (B.) and Lockhart in another paper, and no phosphorescence observed. Consequently kunzite responds only to the γ -rays, which are believed to be virtually Röntgen rays.

6. *Actinium.*—A sample of the still more rare and novel substance discovered by Prof. Debiere (*Comptes Rendus*, cxxix., 593), and received from him through the courtesy of Prof. Curie, was also tried as to its action upon kunzite and some other minerals. The actinium oxide, with an activity of 10,000 according to the uranium standard, gave off profuse emanations and affected diamonds, kunzite, and willemite in a manner similar to the radium salts, with quite as much after-continuance. However, we have not tried the condensation of these emanations upon the minerals by refrigeration.

The peculiar properties of the kunzite variety of spodumene, which have been enumerated, have not been observed in any other of the gem or gem minerals that we have examined. It is barely possible that the small amount of manganese may have much to do with it, but from our present knowledge basing a chemical explanation thereon is idle.—*American Journal of Science*, xviii., p. 25.

NOTICES OF BOOKS

Laboratory Studies for Brewing Students. By ADRIAN J. BROWN, M.Sc. London, New York, and Bombay: Longmans, Green, and Co. 1904.

This book gives a systematic and well-planned guide to the practical work which may advantageously be performed by students of brewing. After studying the structure of the barley-corn, the student proceeds to the examination of the changes occurring in barley during germination and the analysis of malt. In describing the technical methods of examining and valuing malt, and also in other places throughout the book, the author very rightly emphasises the fact that no amount of reading directions from a book can do away with the necessity for instruction by a qualified teacher. The principles of the mashing process are then experimentally examined, the carbohydrates occurring in wort production, and the products of hydrolysis of starch being thoroughly investigated before the student passes to studies bearing more directly on the technological aspect of the brewing process, such as the analysis of beer and of brewing sugars. A few notes on the detection and determination of common adulterants might be useful here. To the subject of fermentation relatively little space is given, in view of the fact that excellent text-books dealing with it exist, and to these references are made when any point requires amplification; however, even as it stands a very satisfactory outlined course is given upon which to build a more detailed study of the physiological aspects of fermentation and the morphology and life-history of the micro-organisms of fermentation. A short chapter on the structure and chemical examination of the hop concludes an excellent book.

Theoretical Chemistry from the Standpoint of Avogadro's Rule and Thermodynamics. By Prof. WALTER NERNST, Ph.D. Revised in Accordance with the Fourth German Edition. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1904.

THE second English edition of Prof. Nernst's valuable treatise has certainly not appeared any too soon, for the original has already run through three editions, and has been altered and improved in many respects by its distinguished author. The English version has been enlarged in accordance with the most recent German edition, which differed from the third chiefly in the inclusion of a chapter on the "Atomistic Theory of Electricity," in which the development of the theory of electrons is discussed, it must be confessed in a somewhat disappointing manner. There is a serious printer's error in the sentence beginning "The electromagnetic theory of light" on page 390, which requires correction, and the whole of this chapter might have been considerably enlarged without giving a dispro-

portionate amount of space to the consideration of a subject of such importance. The treatise undoubtedly forms a useful text-book of theoretical chemistry, both for study and for reference, and the translator's footnotes add to its value in pointing out cases in which Prof. Nernst's views do not coincide with those most generally accepted.

Electric Furnaces and their Industrial Applications. By J. WRIGHT. London: Archibald Constable and Co., Ltd. 1904.

THE increasing use of the electric furnace in various industrial processes makes the appearance of this book particularly timely, and it meets a want in supplying a distinctly readable and descriptive account of the commercial aspects of the subject. From its nature the work can be regarded as a compilation only; it contains abstracts of various papers of importance read before the learned societies, and discussions and descriptions of typical processes and the principles underlying them. The subject is treated pre-eminently from the point of view of the practical man, though a chapter on laboratory furnaces and experimental research is included, in which the furnaces in use at the Owens College and the McGill University are shortly described, and some recent experimental results are discussed. Electrolytic furnaces and processes in which the presence of a fused electrolyte is essential are included, and their treatment forms not the least satisfactory part of the volume.

Manual of Serum Diagnosis. By Dr. O. BOSTOSKI. Authorised Translation by Dr. CHARLES BOLDUAN. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1904.

THE translation of this excellent handbook on serum diagnosis can be recommended to all interested in this branch of serotherapy, and especially to those who wish to keep well abreast of the times. It deals with the diagnosis of typhoid, paratyphoid, tuberculosis, and some other diseases, and also contains chapters on the precipitins as diagnostic reagents and other diagnostic reactions. The translation has been exceedingly well performed, so that the English reader will be at no disadvantage as compared with those who can read the original; and, moreover, the translator has been in correspondence with the author concerning the inclusion of some new matter, most important amongst which is the discussion of Ficker's typhoid diagnostic, which modification of the Gruber-Widal reaction presents special advantages as regards simplicity of manipulation, and appears to be even more reliable than the original reaction.

Die Heterogenen Gleichgewichte vom Standpunkte der Phasenlehre. ("Heterogeneous Equilibria from the Standpoint of the Phase Theory"). By Dr. H. W. BAKHUIS ROOZBOOM. Vol. II. Braunschweig: Friedrich Vieweg und Sohn. 1904.

THE first volume of this work has already been accepted as the standard authority on the subject of the conditions essential for the existence of a heterogeneous system of one component, and this second volume, which deals with two component systems, fully maintains the reputation the first has acquired. The difficulties are of course very much more formidable, but the author's excellent choice of appropriate language and apposite examples does much to lighten the student's labours. The volume treats exclusively of those binary systems in which only the two components appear as solid phases, and is fully illustrated by diagrams; the illustrations of the solid figures which represent graphically the composition of each phase, and the equilibrium, temperature, and pressure being particularly well executed. The depth of the author's knowledge and his peculiar talent for presenting a most difficult subject in the simplest possible manner are apparent throughout this treatise, which deals with a subject whose development he has so greatly furthered.

OBITUARY.

DR. CARL OTTO WEBER.

WE regret to announce that the well-known authority on the chemistry of indiarubber, Dr. Carl Otto Weber, died suddenly at his residence in Massachusetts, U.S.A., on the 14th inst.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxxxix., No. 26, December 26, 1904.

Constitution of Sodium Salts of certain Methenic and Methinic Acids. Cyanacetic, Acetylcyanacetic, Malonic, and Cyanomalonic Ethers. Malonitrile and Cyano-camphor.—A. Haller and P. Th. Muller.—The research described in the present paper is a continuation of one recently published on certain acetylcyanacetic ethers. For some time it has been uncertain whether, in the sodium salts of certain ethers, the alkaline metal is united to the carbon or to the oxygen. The authors endeavour to solve this problem by means of the differential optical method which M. Muller previously used for the diagnosis of the pseudo-acids. By this method the molecular refraction of the sodium salt and that of the generating acid are compared, as far as possible using the same solvent and equal concentrations. The normal acids (carboxylic acids and cacodylic acid) give for the D line a difference (Δ) lying between 1.4 and 1.9, and always less than 2. In the case of the pseudo-acids the value is always above 2, indicating that the salt has a different constitution from the corresponding acid. A list of tables are given showing values for the sodium salts of the acetylcyanacetic and cyanomalonic ethers.

Quadrivalent Oxygen.—E. E. Blaise.—The author investigates the variation in the basicity of the oxygen atom according to the weight of the carbon radicles to which it is linked. He discovers that the atom of oxygen behaves as if it were more basic as the radicles are heavier. Amyl oxide, for example, displaces ethyl oxide in an iodomagnesium compound with great energy. If, on the contrary, the radicle attached to the oxygen in the ether oxide is cyclic, the acidity of this radicle intervenes and diminishes the basicity of the oxygen. For this reason ethyl oxide displaces anisol—a reaction showing itself by the abundant crystallisation of magnesium etheriodide.

Reduction of Bibasic Acid Anhydrides.—G. Blanc.—The facility with which the groups $\text{—COOC}_2\text{H}_5$ and —CONH_2 are reduced to the group $\text{—CH}_2\text{OH}$ by sodium and absolute alcohol, led the author to try this method of obtaining the lactones starting from bibasic acid anhydrides, with the purpose of replacing the old method of preparation by sodium amalgam and aluminium amalgam by a more practical one. This theory also predicted that, if dissymmetric acid anhydride is used, it is impossible by the old methods to discover on which side the reduction occurs. Experiment proves that by the author's new method this uncertainty disappears.

General Method of Synthesis of Aldehydes by means of Substituted Glycidic Acids.—Georges Darzens.—The author first prepares the ethers of the β -disubstituted glycidic acids. These ethers are saponified, and very stable alkaline salts are prepared, soluble in water. From the aqueous solution the corresponding acid can be precipitated by a mineral acid. The free disubstituted glycidic acids are not stable, and decompose very readily into carbon dioxide and the aldehydes.

MISCELLANEOUS.

Leconte Prize.—M. René Blondlot was awarded the Leconte Prize in 1904 by the Académie. His chief work during recent years is on the peculiar actions which he attributes to a new radiation called by him N-rays. All the properties of these newly discovered rays have not yet been investigated. His other researches have been on the comparative rapidity of transmission of light and electricity. He also made various experiments on the Hertzian waves.

Institute of Chemistry.—Pass List of the January Examinations.—Of 18 Candidates who entered for the Intermediate Examination, the following thirteen passed:—S. J. M. Auld, Ph.D (Würzburg); S. L. Archbutt; A. W. Bain, B.A., B.Sc. (Lond.); J. T. Cart, B.Sc. (Lond.); T. F. Cowie; D. Gair, B.Sc. (Lond.); C. T. Gimingham; H. G. Harrison, B.A. (Cantab.); Elsie S. Hooper, B.Sc. (Lond.); S. G. Liversedge; W. H. Simmons, B.Sc. (Lond.); A. S. Stockwin, B.Sc. (Lond.); and E. J. Wilson, B.A. (Cantab.). In the Final Examination for the Associateship (A.I.C.) in Mineral Chemistry, of six who entered the following five passed:—H. Calam, B.Sc. (Vict.); J. D. Fraser; R. F. Korte, Ph.D. (Heidelberg); W. D. Rogers, Assoc.R.C.Sc. (Lond.); and P. E. Spielmann, Assoc.R.C.Sc. (Lond.). Of three Candidates in Organic Chemistry, one passed:—H. E. Laws, B.Sc. (Lond.). Of the nine who entered in the Branch of the Analysis of Food and Drugs, and of Water, including an Examination in Therapeutics, Pharmacology, and Microscopy, the following six passed:—G. S. A. Caines; S. W. Collins; R. M. Filmer; H. E. Gresham, B.Sc. (Lond.); V. H. Kirkham, B.Sc. (Lond.); and J. Miller. One Candidate passed a General Practical Examination for the Fellowship (F.I.C.):—W. H. Merrett, A.R.S.M. The Examiners in Chemistry were Mr. W. W. Fisher, M.A. (Oxon.), F.I.C., and Dr. G. G. Henderson, M.A., F.I.C. Dr. A. P. Luff conducted the Examination in Therapeutics, Pharmacology, and Microscopy.

MEETINGS FOR THE WEEK.

- MONDAY, 30th.**—Society of Arts, 8. (Cantor Lecture), "Reservoir, Stylographic, and Fountain Pens," by James P. Maginnis, Assoc.M.Inst.C.E., &c.
— Faraday Society, 8. "Mass Analyses of Muntz's Metal by Electrolysis, and some Notes on the Electrolytic Properties of this Alloy," by J. G. A. Rhodin. "The Equilibrium between Sodium and Magnesium Sulphates," by R. B. Denison. "Refractory Materials," by E. K. Scott.
- TUESDAY, 31st.**—Royal Institution, 5. "The Structure and Life of Animals," by Prof. L. C. Miall, D.Sc., F.R.S.
— Society of Arts, 8. "Calligraphy and Illumination," by Edward Johnston and Graily Hewitt.
- WEDNESDAY, Feb. 1st.**—Society of Arts, 8. "The Navigation of the Nile," by Sir William H. Preece, K.C.B., F.R.S.
- THURSDAY, 2nd.**—Royal Institution, 5. "Forestry in the British Empire," by Prof. W. Schlich, F.R.S., &c.
— Chemical, 8. "Studies in the Camphane Series—Part XVI., Camphorylcarbimide and Isomeric Camphorylcarbimides," by M. O. Forster and H. E. Pierz.
- FRIDAY, 3rd.**—Royal Institution, 9. "Blood Pressure in Man," by Prof. T. Clifford Allbutt, F.R.S., &c.
- SATURDAY, 4th.**—Royal Institution, 3. "The Bobemian School of Music" (with Musical Illustrations), by Sir Alexander Mackenzie, Mus.Doc., D.C.L., LL.D.

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DAY and EVENING SCIENCE CLASSES—

CHEMISTRY J. E. MACKENZIE, Ph.D., D.Sc.
PHYSICS A. GRIFFITHS, D.Sc.
MATHEMATICS E. H. SMART, M.A.
BOTANY A. B. RENDLE, M.A., D.Sc.
ZOOLOGY H. W. UNTHANK, B.A., B.Sc.
GEOLOGY & MINERALOGY G. F. HARRIS, F.G.S.
METALLURGY, MINING,
and ASSAYING .. G. PATCHIN, A.R.S.M.

Classes in FRENCH, GERMAN, SPANISH, RUSSIAN, ITALIAN, DUTCH.

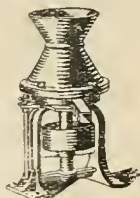
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THE CHEMICAL NEWS.

VOL. XCI., No. 2358.

NOTE ON THE CAUSE OF THE PERIOD OF CHEMICAL INDUCTION IN THE UNION OF HYDROGEN AND CHLORINE.*

By D. L. CHAPMAN and C. H. BURGESS,
Demonstrators in Chemistry in the University of Manchester.

THE induction period, which, in certain circumstances, is observed when a mixture of hydrogen and chlorine is exposed to light, has been commonly attributed to the preliminary formation of an unstable intermediate compound. The authors have for some time held that this view does not accord with the observed facts. This contention is confirmed by recent experiments, which have established that the phenomenon in question is due to the presence in the gas (or in the aqueous solution in contact with it) of substances capable of reacting with chlorine.

At an early stage in the investigation, it was proved that the retardation of chemical action did not depend on any condition of the hydrogen, thus making it only necessary to consider the condition of the chlorine itself, and of the other substances immediately in contact with it.

Water, and particularly solutions of salts in water, possess the power of rendering active chlorine inactive towards hydrogen. On long contact with chlorine in the presence of light, or on boiling with chlorine, these solutions lose this property, even after subsequent removal of the chlorine by exhaustion. Numerous experiments have recently been made in order to find out if these solutions recover their power of rendering chlorine inactive, and it has been found that the only method of effecting this is by the introduction of substances which react with chlorine. Of the compounds investigated, the most efficient to use for this purpose is ammonia, minute traces of which are capable of preventing the action between hydrogen and chlorine for a period of time many times longer than had been previously observed. Sulphur dioxide acts in the same sense as ammonia, but it is more easily removed on exposure to light.

It has been hitherto supposed that an active mixture of hydrogen and chlorine, after standing in the dark for several hours, returned to its original inactive condition. If this were really the case it would be an objection to the view that the induction period is due to the presence of impurities. By the employment of a quartz actinometer, we have, however, succeeded in showing that no decay of activity takes place: and, after keeping the mixture for days in the dark, the gases immediately combine on exposure to light—without any period of gradual acceleration.

Metallic Calcium.—K. Arndt.—The specific gravity of a specimen of metallic calcium obtained from the electro-chemical works at Bitterfeld was found to be 1.54, rising to 1.56 after the metal had been fused, while a specimen prepared by the author himself gave 1.59. This difference was to be ascribed to the higher percentage of silicon in the latter (1.1 per cent as compared with 0.6 per cent Si). Another specimen, containing 0.5 per cent Si, had the specific gravity 1.577. Thus, it appeared from these results that the specific gravity of pure calcium must be less than 1.54, and for distilled calcium it was found (by the method of suspension in a mixture of chloroform and ethyl iodide) to be 1.52. The melting point *in vacuo* appears to be about 800°, and below this point it begins to pass into vapour, and is deposited in fine crystals. The vapour reacts very readily with air, giving CaO and Ca₃N₂. Solid calcium reacts similarly, but far more slowly.—*Berichte*, xxxviii., No. 18.

HYDROLYSIS OF CANE-SUGAR BY *d*- AND *l*-CAMPHOR- β -SULPHONIC ACID.*

By ROBERT JOHN CALDWELL, B.Sc., Clothworkers' Scholar,
Chemical Department, City and Guilds of London Institute,
Central Technical College.

THE study of the action of asymmetric hydrolytic agents on the sugars acquires interest from the fact that enzymes, which exhibit most remarkable activity as hydrolysts, are apparently all asymmetric in structure. The only experiments of the kind made hitherto are those by Emil Fischer (*Zeits. Physiol. Chem.*, 1898, vol. xxvii., p. 83), on the action of *d*- and *l*-camphoric acids on cane-sugar, described in his memoir on the importance to Physiology of Stereochemistry. No difference was detected; but as the experiments were made at 90° C. in sealed tubes, it was desirable to extend the inquiry and to operate under conditions more nearly comparable with those under which enzymes act.

At Prof. Armstrong's suggestion, the acids selected for the purpose were the two isomeric acids of opposite activity prepared by direct sulphonation of *d*- and *l*-camphor by Reychler's method. They are easily prepared and they act quickly, so that their action can be studied at atmospheric temperatures; moreover, as concentrated solutions can be used, even a small difference in their activity should not escape detection. The inversion was carried out in a polarimeter tube enclosed in a jacket through which a flow of water was maintained varying in temperature by only $\pm 0.05^\circ$ from 20.05° C. Readings on α_D were taken at intervals of fifteen minutes. The results obtained are entered in the following tables, in which *a* is the amount of cane-sugar per litre of solution when the first reading was taken, and *a* - *x* the concentration of the solution, at other times *t* minutes after the first reading. The strength of the acid in all cases was 0.488 gm. molecule per litre, as determined by titration with alkali. The concentration of the sugar solution used was 17.1 per cent (0.5 gm. molecule). The rate of change was such that the inversion was about half completed at the end of six hours; the end point was determined in Cases I. and II. after forty-eight hours standing at 20° C.

Although there cannot have been any great difference in the conditions in the different experiments, the results must not all be included in one series, as the temperature regulator was re-adjusted after the first and after the fourth experiment; they are therefore to be considered in three sets, viz., I.; II., III., IV.; V., VI., VII., VIII.

The first set gave $K = 10.02$ for the dextro acid, and 9.95 for the laevo acid; in the second set, the value obtained for the dextro acid was 9.87, that for the laevo acid being 9.99.

Slight variations in the temperature would account for such differences, as the influence of temperature on the rate of change is known to be very great. But even in these experiments the variations observed are small, and not such as to suggest any substantial difference between the two acids. In the last set of observations, fully set forth in the table, which there is every reason to regard as satisfactory, there is clearly no evidence of a difference in the activity of the *d*- and *l*-acids to be noticed.

The results, therefore, not only confirm the conclusion arrived at by E. Fischer, but are also in agreement with the observations of Marckwald and Chwolle (*Ber.*, 1898, vol. xxxi., p. 783), that methylic *d*- and *l*-tartrates are hydrolysed with equal readiness by *l*-nicotine (at 17.5 and 40° C.). On the other hand, they are in remarkable contrast with the conclusions of Marckwald and McKenzie (*Ber.*, 1899, vol. xxxii., p. 3120), and of McKenzie (*Trans. Chem. Soc.*, 1904, vol. lxxxv., p. 378), that ethereal salts similarly derived from optically active isomeric compounds are both formed and hydrolysed at different rates. It is to be noticed, however, that the experiments of these chemists were carried out at relatively high temperatures, and that they involved racemisation.

* A Paper read before the Royal Society, January 26, 1905.

A Paper communicated to the Royal Society, June 16 1904

TABLE II.

Time.	V. Dextro-acid.			VI. Lævo-acid.			VII. Dextro-acid.			VIII. Lævo-acid.		
	ao.	$\frac{10^4}{t} \log_{10} \frac{a}{a-x}$		ao.	$\frac{10^4}{t} \log_{10} \frac{a}{a-x}$		ao.	$\frac{10^4}{t} \log_{10} \frac{a}{a-x}$		ao.	$\frac{10^4}{t} \log_{10} \frac{a}{a-x}$	
15	26.65	—		16.70	—		26.70	—		16.73	—	
30	25.68	9.86		15.67	[10.45]		25.67	[10.46]		15.68	[10.65]	
45	24.70	10.08		14.75	10.06		24.75	10.07		14.73	10.31	
60	23.80	9.99		13.82	10.07		23.80	10.15		13.85	10.06	
75	22.88	10.09		12.93	10.06		22.95	10.01		12.93	10.14	
90	22.00	10.13		12.07	10.05		22.05	10.11		12.03	10.21	
105	21.18	10.09		11.25	10.03		21.22	10.09		11.18	10.22	
120	20.22	10.08		10.43	10.06		20.38	10.16		10.47	10.02	
135	19.57	10.14		9.65	10.06		19.65	10.07		9.67	10.06	
150	18.88	10.04		8.88	10.09		18.85	10.14		8.92	10.06	
165	18.15	10.05		8.18	10.05		18.17	10.07		8.18	10.08	
180	17.45	10.05		7.47	10.06		17.45	10.10		7.50	10.05	
195	16.75	10.08		6.82	10.03		16.72	10.16		6.82	10.05	
210	16.12	10.06		6.17	10.03		16.07	10.16		6.17	10.05	
225	15.48	10.07		5.47	10.11		15.40	10.15		5.57	10.01	
240	14.85	10.08		4.92	10.04		14.80	10.18		4.93	10.05	
255	14.27	10.08		4.32	10.05		14.22	10.17		4.33	10.06	
270	13.65	10.14		3.73	10.07		13.67	10.15		3.83	9.99	
285	13.12	10.12		3.20	10.05		13.15	10.11		3.25	10.02	
300	12.60	10.11		2.73	9.99		12.53	10.20		2.70	10.04	
315	12.05	10.14		—	—		12.05	10.17		2.22	10.00	
345	—	—		1.18	10.06		—	—		—	—	
Complete change	-2.33	—		-12.35	—		-2.33	—		-12.35	—	
Mean..	—	10.07		—	10.07		—	10.13		—	10.08	

An experiment made with chlorhydric acid and cane-sugar under conditions precisely similar to those prevailing in Experiments V.—VIII. (Table II.), using a solution containing 17.6 per cent (0.5 gram. molecule) of cane-sugar and 0.486 gram. molecule of hydrogen chloride, gave the value $K = 11.18$.

Representing the activity of hydrogen chloride as 100, that of camphor- β -sulphonic acid is therefore 89.8, which is a value in accord with that assigned by Ostwald to ethylsulphonic acid, viz., 91.2.

In the preliminary stage of the inquiry, a comparison was also made of the action of chlorhydric acid and of *d*-camphor- β -sulphonic acid on milk-sugar at 60.1°. The value obtained for the former was $K = 3.53$ (*Proc. Roy. Soc.*, vol. lxxiii., p. 532). The values observed in the case of the camphor-acid are given in Table I.

TABLE I.—Eighteen per cent (0.5 gram. molecule) Milk-sugar, 0.400 gram. molecule *d*-Camphor- β -sulphonic Acid. Temperature, 60.1°.

Time, in hours.	ao.	Per cent hydrolysed.	$\frac{10^4}{t} \log_{10} \frac{a}{a-x}$
0	20.90	—	—
8	21.73	14.9	[1.46]
16	21.93	18.5	0.93
22	22.37	26.4	1.01
44	23.45	45.8	1.01
72	24.30	61.0	0.95
95	24.88	71.5	0.96
Complete change	26.47	Mean ..	0.97

K (for normal acid) = 2.43.

Although possibly affected by a considerable error, on account of the difficulty attending such observations at high temperatures, these results appear to indicate that the activities of the two acids are by no means the same towards cane-sugar and towards milk-sugar, being about 100 : 90 in the one case and 100 : 70 in the other. Sigmond has already shown (*Zeit. Phys. Chem.*, 1898, vol. xxvii., p. 390) in the case of cane-sugar and maltose, that although sulphuric and oxalic acids have the same relative activity towards both carbohydrates, chlorhydric acid is relatively

more active towards maltose; it appears, therefore, that cane-sugar is less sensitive to attack by chlorhydric acid than are other sugars. The point is one which deserves further investigation.

Although the experiments described in this note have given a negative answer to the question considered, it is proposed to extend the inquiry to other acids.

ON SOME CUPRAMMONIUM SULPHATES.*

By DAVID W. HORN and EDYTHA E. TAYLOR.

THE extensive investigations recently carried out on solutions of cuprammonium salts have made it desirable that the salts themselves be isolated and studied. This paper deals mostly with the cuprammonium sulphate longest known among the metal-ammonium compounds, $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$, and the decomposition-products that have been given the formulæ $\text{CuSO}_4 + 2\text{NH}_3$ and $\text{CuSO}_4 + \text{NH}_3$. Of these formulæ, $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ has rested upon one analysis made by Berzelius (*Gilbert's Ann.*, xl., 300) of apparently the same salt to which Bouzat has but recently (*Ann. Chim., Phys.*, 1903, [7], xxix., 305) assigned a different formula— $\text{CuSO}_4 + 4\text{NH}_3 + 3/2\text{H}_2\text{O}$. The formulæ $\text{CuSO}_4 + 2\text{NH}_3$ and $\text{CuSO}_4 + \text{NH}_3$ have no basis in fact except the losses in weight observed by Kane (*Ann. Chim. Phys.*, [2], lxxii., 265) when the salt stated by Berzelius to be $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ is heated at different temperatures. Changes in weight cannot be relied upon to differentiate ammonia having a molecular weight of 17 from water having a molecular weight of 18, even when the original substance is known to have a definite composition. For these reasons we proposed to prepare these substances, insuring the reliability of our preparations by complete analyses. Such analyses involve the difficulty of determining ammonia and water in a mixture of the vapours of the two, as well as that of determining sulphuric acid in copper compounds. We worked out reliable analytical

* From the *American Chemical Journal*, xxxii., No. 3.

methods, and then studied the preparation and properties of the salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$, its behaviour at elevated temperatures, and the properties of its aqueous solution. This paper presents these points in order.

I. Analytical Methods.

A. *Determination of Copper*.—We first tried a rapid electrolytic method proposed by Wagner for the determination of copper (*Zeit. Elektrotech. u. Elektrochem.*, ii., 613—616). The deposits were not uniform, but contained here and there brownish lumps. When the electrolysis was pushed so far that hydrogen sulphide no longer gave a precipitate in the liquid that was being electrolysed, the results were high. This is illustrated by the following analysis:—

Weight of salt taken for analysis.	Weight of copper found.	Percentage of copper found.	Percentage of copper calculated for $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$.
Grm.	Grm.		
1.0081	0.2621	25.99	25.86

We then adopted Rose's method of heating the dehydrated sulphates with sulphur in an atmosphere of hydrogen (*Anal. Chem.*, II., 173—4, sixth German edition). The following analyses are given to show the degree of accuracy of the method:—

Weight of salt taken for analysis.	Weight of copper found.	Percentage of copper found.	Percentage of copper calculated for $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$.
Grm.	Grm.		
0.5419	0.1401	25.87	25.86
0.4059	0.1049	25.87	
0.7004	0.1812	25.87	
0.5650	0.1463	25.89	
0.3632	0.0939	25.86	
0.5382	0.1392	25.87	
0.2811	0.0726	25.83	
0.4356	0.1126	25.86	
0.3921	0.1014	25.89	
0.4914	0.1271	25.84	
0.3146	0.0813	25.84	
0.3710	0.0960	25.87	

B. *Determination of Ammonia*.—The usual method of distillation with an alkali was used. When the alkali was previously treated with potassium permanganate the results were invariably low in the case of copper compounds, although when ammonium borate was used to test the method the results were good. We used sodium hydroxide free from nitrogen. Lime was added to the alkaline liquids to prevent "bumping" during the distillations. It was found that the ammonia could only be completely removed from the copper compounds when the distillations were continued until the residues in the distilling-flasks reached approximately the concentration of 1 grm. sodium hydroxide in 1 c.c. to 1.5 c.c. of the liquid. In order to prevent the mechanical carrying-over of alkali in the distillations we found it advisable to use long-necked balloon-flasks of about 2.5 litres capacity, and to distil at such a rate that the condenser-tube was but one-fourth to one-third full of uncondensed water-vapour. To avoid loss of ammonia, the salts were weighed into a slight excess of acid contained in the distilling-flasks. The following analyses of the salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ show to what extent the method can be relied upon when the precautions mentioned are taken:—

Weight of salt taken for analysis.	Weight of ammonia found.	Percentage of ammonia found.	Percentage of ammonia calculated for $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$.
Grm.	Grm.		
0.3521	0.0980	27.82	27.76
0.3969	0.1099	27.70	
0.2974	0.0825	27.76	
0.5006	0.1393	27.82	
0.3806	0.1057	27.77	
0.3049	0.0844	27.71	
0.4766	0.1322	27.74	

As already mentioned, ammonium borate may be used advantageously in testing the apparatus in the distillations, because the ammonia in it can be determined by direct titration as well as by distillation.

C. *Determination of Water and Ammonia*.—Water and ammonia are evolved simultaneously by the salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ when it is heated. We determined them by heating a weighed quantity of the salt in a boat in a tube so arranged that a current of air, dry and free from carbon dioxide, could pass over the heated material and carry the water and ammonia evolved into absorption apparatus. We used air that had been passed through dilute sulphuric acid and barium hydroxide solutions, and then over solid sodium hydroxide and potassium hydroxide. The air leaving this apparatus entered the tube containing the boat through a piece of ordinary glass tubing about 2 metres long. The end of this connecting tube nearest the boat was drawn to a capillary tip in order to prevent as far as possible the diffusion of the ammonia backward toward the apparatus for purifying the air. The larger tube, in which the boat was heated, was placed in a cylindrical air-bath of about four times the length of the boat. This tube was joined directly to the absorption-apparatus consisting of two glass-stoppered U-tubes filled with solid potassium hydroxide to absorb the water evolved, and a similar tube containing glass beads and 65 per cent sulphuric acid (to absorb the ammonia) joined with two more tubes of potassium hydroxide to absorb the water given off by the acid. We tested this apparatus and method for the determination of water, using crystallised barium chloride, the loss in weight of the boat checking on the changes in weight in the absorption-tubes. There was no occasion to test the absorption of ammonia by the acid. The results of eight analyses made by this method will be given later on.

The current of air used in these and other similar experiments was furnished by a simple apparatus that has since been found so useful in the laboratory that it will be described. A Bunsen pump passing through a rubber stopper is fitted into the middle opening of a Wolff bottle; into one of the side openings a syphon-tube is fitted by a rubber stopper, the arm of the tube within the bottle reaching almost to the bottom of the bottle; into the other opening there is fitted a tube bent at a right angle, and cut off just beneath the rubber stopper through which it passes. The pump supplies water and air, the former being drawn off or forced out through the syphon-tube, and the latter being drawn as needed from the other (outlet) tube. In using this apparatus the only precaution to be observed is that neither water nor air be drawn off faster than it is supplied by the pump. If the outlet of the syphon-tube be small, the air is supplied under considerable pressure.

D. *Determination of Sulphuric Acid*.—Precipitated barium sulphate "carries down" copper salts perhaps more freely than it does iron salts (Berzelius, *Ann. Chim. Phys.*, [2], xiv., 376). For this reason it is imperative that the copper and sulphuric acid be separated quantitatively, leaving the latter under such conditions that it can be precipitated as (relatively) pure barium sulphate.

It is apparent that, in this case, the copper cannot be precipitated as sulphide. Gibbs proposed to precipitate copper with sodium carbonate (*Zeit. Anal. Chem.*, vii., 258). We precipitated copper by this method, as directed in Fresenius's "Quantitative Analysis" (sixth German edition, I., 331), after we had treated the salt with a slight excess of dilute hydrochloric acid. The following were the results obtained by the careful precipitation of barium sulphate in the filtrates from the copper precipitates after an excess of hydrochloric acid had been added to these filtrates:—

Weight of salt taken for analysis.	Weight of SO_4 found.	Percentage of SO_4 found.	Percentage of SO_4 calculated for $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$.
Grm.	Grm.		
0.2832	0.0825	29.12	30.06
0.3666	0.1076	29.36	
0.2522	0.0763	30.25	
0.3754	0.1108	29.52	

These figures showed that the precipitates contained sulphuric acid, which had been retained although the precipitates had been washed until the wash-waters no longer reacted with barium chloride. The presence of sulphuric acid in similar precipitates was proven later by qualitative tests, which also showed that the precipitates consisted partly of carbonates. The four original precipitates were analysed for copper by Rose's method. The results showed the completeness of the previous precipitations of copper, and that the precipitates could be washed free from alkali salts; they also served, along with the sulphuric acid determinations already given, to show that the proportion of copper to sulphuric acid in the (Gibbs) precipitates is very approximately 4 : 1.

Number of precipitate taken.	Weight of copper found. Gm.	Percentage of copper found in salt.	Percentage of copper calculated for $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$.
1.	0.0733	25.87	25.86
2.	0.0952	25.97	
3.	0.0651	25.93	
4.	0.0791	25.87	

The advantages of Gibbs's method for precipitating copper are sufficiently clear. However, it cannot be used to separate sulphuric acid from copper because the green precipitate contains one equivalent of sulphuric acid to every four of copper present.

The copper was next precipitated as hydroxide by the addition of caustic potash to solutions of the salt (previously made slightly acid with hydrochloric acid), according to the directions of Fresenius (*loc. cit.*, p. 329). The precipitates were difficult to wash, and when tested qualitatively were always found to contain sulphuric acid, although the wash-waters from them had no longer reacted with barium chloride. The following analyses (1—4) of the precipitates for copper by Rose's method show that they had probably retained alkali salts in addition to the sulphuric acid already mentioned; analyses 5 and 6 were made by applying Rose's method to the original salt, and are given for comparison:—

Number of analysis.	Weight of salt taken for analysis. Gm.	Weight of copper found. Gm.	Percentage of copper found.	Percentage of copper calculated for $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$.
1.	0.3474	0.0913	26.23	25.86
2.	0.4444	0.1168	26.28	
3.	0.6471	0.1690	26.11	
4.	0.5107	0.1337	26.17	
5.	0.3146	0.0813	25.84	
6.	0.3546	0.0916	25.85	

We next tried adding the solution of the copper salt, previously acidified with hydrochloric acid, to an excess of caustic soda. The precipitates thus formed are comparatively easily washed, and afterward do not contain any sulphuric acid. Further, in this procedure it is not necessary to use a large excess of alkali, so that after the filtrates have been acidified and before the sulphuric acid in them is precipitated they contain comparatively small amounts of alkali salts. This is an advantage, because alkali salts are also "carried down" by barium sulphate. There is a further advantage in using caustic soda, for potassium salts are "carried down" in larger quantities than sodium salts (Kretschy, *Zeit. Anal. Chem.*, x., 396). The results given later on show the degree of accuracy of this method. In detail, the procedure was as follows:—

A quantity of the copper salt containing about 0.09 gm. of copper was weighed into a small beaker containing about 50 c.c. of water. Hydrochloric acid was then added until the precipitate at first formed had completely redissolved. About 150 c.c. of a solution of sodium hydroxide (free from sulphates), containing 2 grms. of sodium hydroxide per litre, were heated to boiling in a large beaker. The copper solution was slowly stirred into the boiling liquid, the transfer being completed with water.

The mixture was boiled gently for a few minutes, and then digested for about half-an-hour just below the boiling temperature. The solution was filtered while hot. The precipitate, which had been retained in the beaker, was washed four times by decantation with hot water; it was then transferred to the filter and again washed with hot water until the wash-waters did not give a precipitate with barium chloride. The precipitate was then tested for sulphuric acid after it had been dissolved in dilute hydrochloric acid. The entire filtrate was acidified with hydrochloric acid and treated with an excess of barium chloride, observing the well-known precautions. The barium sulphate was treated as is usual.

The suggestion of Küster and Thiel to "remove the ion" (*Zeit. Anorg. Chem.*, xix., 99) that interferes in precipitations of barium sulphate was tried in each of the above cases. The following are the records of the experiments:—

I. Copper was precipitated by sodium carbonate, an excess of barium chloride was added to the hot mixture, and then an excess of hydrochloric acid was added to dissolve the copper precipitate. The barium sulphate was digested with the acid solution about half-an-hour, and then collected and treated as usual. The results are among those given below, and are numbered 1 and 2.

II. Copper was precipitated by adding caustic potash; the rest of the treatment was as in I. The results are numbered 3 and 4.

III. Copper was precipitated by adding the solution containing it to an excess of caustic soda; the rest of the treatment was as in I. The results are numbered 5 and 6.

Number of analysis.	Weight of salt taken for analysis. Gm.	Weight of SO_4 found. Gm.	Percentage of SO_4 found.	Percentage of SO_4 calculated for $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$.
1.	0.2611	0.1068	40.91	39.06
2.	0.2548	0.1047	41.11	
3.	0.2642	0.1052	39.83	
4.	0.2757	0.1087	39.44	
5.	0.2135	0.0847	39.67	
6.	0.2088	0.0832	39.84	

In our opinion the method of Küster and Thiel is not applicable in the presence of copper.

(To be continued).

MEETING OF THE BRITISH ASSOCIATION IN SOUTH AFRICA.

THE British Association holds its meeting this year in South Africa. Under these exceptional circumstances, the general officers of the Association requested the Council to appoint a strong Committee to co-operate with them in carrying out the necessary arrangements. This South African Committee has held frequent sittings, and their work is so far advanced that it is now possible to make the following announcements.

Although the annual circular and programme have not yet been issued, pending the receipt of information from South Africa, many members have already intimated their intention of being present at the meeting. The Official Party of guests invited by the Central Executive Committee at Cape Town, and nominated in the first instance by the Council of the Association, numbers upwards of 150 persons, comprising members of the Council, past and present General Officers and Sectional Presidents, the present Sectional Officers, and a certain proportion of the leading members of each Section. To this list has yet to be added, on the nomination of the organising committees, the names of representative foreign and colonial men of science, the total number of the Official Party being restricted to 200, including the local officials. It is hoped, however, that

many other members of the Association will also attend the meeting.

The Presidents-elect of the various Sections are as follows:—

- A (Mathematical and Physical Science)—Prof. A. R. Forsyth, M.A., Sc.D., F.R.S.
- B (Chemistry)—G. T. Beilby.
- C (Geology)—Prof. H. A. Miers, M.A., D.Sc., F.R.S.
- D (Zoology)—G. A. Boulenger, F.R.S.
- E (Geography)—Admiral Sir W. J. L. Wharton, K.C.B., F.R.S.
- F (Economic Science and Statistics) — Rev. W. Cunningham, D.D., D.Sc.
- G (Engineering)—Colonel Sir Colin Scott-Moncrieff, G.C.S.I., K.C.M.G., R.E.
- H (Anthropology)—A. C. Haddon, M.A., Sc.D., F.R.S.
- I (Physiology)—Colonel D. Bruce, M.B., F.R.S.
- K (Botany)—Harold Wager, F.R.S.
- L (Educational Science)—Sir Richard C. Jebb, Litt.D., M.P.

The Vice-Presidents, Recorders, and Secretaries of the eleven Sections have also now been appointed.

In view of the numerous towns to be visited by the Association, and in which lectures or addresses will be given, the number of Lecturers appointed is much larger than usual. The list of these, as at present arranged, is as follows:—

- Cape Town.*—Prof. Poulton, on Burchell's work in South Africa; and Mr. C. V. Boys, on a subject in Physics.
- Durban.*—Mr. F. Soddy, on Radio-activity.
- Maritzburg.*—Prof. Arnold, on Compounds of Steel.
- Johannesburg.*—Prof. Ayrton, on Distribution of Power; Prof. Porter, on Mining; and Mr. G. W. Lamplugh, on the Geology of the Victoria Falls.
- Pretoria* (or possibly *Bulawayo*).—Mr. Shipley, on a subject in Zoology.
- Bloemfontein.*—Mr. Hinks, on a subject in Astronomy.
- Kimberley.*—Sir William Crookes, on Diamonds.

As the wish has been conveyed to the Council, from South Africa, that a few competent investigators should be selected to deliver addresses dealing with local problems of which they possessed special knowledge, a geologist, a bacteriologist, and an archaeologist have been invited to undertake this work, involving in two cases special missions in advance of the main party. Whilst Colonel Bruce, F.R.S., will deal with some bacteriological questions of practical importance to South Africa, Mr. G. W. Lamplugh (by the courtesy of the Board of Education) will be enabled to investigate certain features in the Geology of the Victoria Falls—particularly as regards the origin and structure of the Cañon—and Mr. D. R. MacIver, who is at present exploring in Nubia, will proceed in March to Rhodesia, in order to examine and report on the ancient ruins at Zimbabwe, and also Inyanga.

Most of the officials, and other members of the Association, will leave Southampton on July 29, by the Union-Castle mail s.s. *Saxon*, and arrive at Cape Town on August 15, the opening day of the meeting, but a considerable number will start from Southampton on the previous Saturday, either by the ordinary mail-boat or by the intermediate steamer sailing on that date.

The Sectional Meetings will be held at Cape Town (three days) and Johannesburg (three days). Between the Inaugural Meeting at the former and the concluding meeting at the latter town, opportunities will be offered to members to visit the Natal Battlefields and other places of interest. Subsequently, a party will be made up to proceed to the Victoria Falls (Zambesi); and, should a sufficient number of members register their names, a special steamer will be chartered for the voyage home, via Beira, by the East Coast Route, as an alternative to the return through Cape Town by the West Coast Route. Thus, all the Colonies and Rhodesia will be visited by the Association. The tour will last 70 days via Cape Town,

or a week longer via Beira (all sea), leaving Southampton on July 29, and returning thither on October 7 or October 14.

A Central Executive Committee has been constituted at Cape Town, with Sir David Gill as Chairman, and Dr. Gilchrist as Secretary, while Local Committees have been formed at Johannesburg and other important centres.

Prof. G. H. Darwin, F.R.S., is the President-elect; and among the Vice-Presidents-elect are the following:—The Rt. Hon. Lord Milner, the Hon. Sir Walter Hely-Hutchinson, Sir Henry McCallum, the Hon. Sir Arthur Lawley, Sir H. J. Gould-Adams, Sir David Gill, and Sir Charles Metcalfe.

Sir David Gill, Mr. Theodore Reunert, and others have taken a prominent part in the initial work. The South African Association for the Advancement of Science are cordially co-operating in the local organisation, and will join with the British Association in attending the meeting.

The aim of the Council has been to secure the attendance of a representative body of British men of science, including specialists in various lines of investigation, and that, along with the generous support of the people and authorities in South Africa, should go far to ensure the success of the meeting and to stimulate local scientific interest and research.

THE IRON AND STEEL INSTITUTE.

THE Annual General Meeting of the Iron and Steel Institute will be held at the Institution of Civil Engineers, on Thursday and Friday, May 11 and 12, 1905. The Annual Dinner will be held, under the presidency of Mr. R. A. Hadfield, in the Grand Hall of the Hotel Cecil, on Friday, May 12.

The Council will shortly proceed to award Carnegie Research Scholarships, and candidates must apply before February 28. The awards will be announced at the General Meeting.

The Autumn Meeting will be held in Sheffield, on September 25 to 29, 1905. An influential Committee has been formed in Sheffield for the reception of the Institute, with the Lord Mayor as Chairman, and the Master Cutler as Vice-Chairman.

Members are invited to participate in an International Congress of Mining, Metallurgy, Mechanics, and Applied Geology, to be held at Liège, on June 26 to July 1, 1905, in connection with the International Exhibition. The subscription to the Congress is 25 francs (£1), and members should enter their names in that section of which they wish to receive the publications. The General Secretary of the Organising Committee is M. Henri Dechamps, 16, Quai de l'Université, Liège. The subjects to be dealt with in the Metallurgical Section comprise coke manufacture; blast-furnace practice; influence of titanium, arsenic, and other substances on iron and steel; removal of dust from blast-furnace gas; slag cement; use of poor gas as motive power in rolling-mills; new methods of open-hearth steel manufacture; alloys of steel with chromium, nickel, manganese, vanadium, and tungsten; the forging press and steam hammer; electro-metallurgy, and the practical applications of metallography. Visits to the Exhibition, and to scientific and industrial establishments will be arranged.

Royal Institution.—Prof. G. H. Bryan being unable to lecture on Friday evening, March 24, Sir Oliver Lodge, LL.D., D.Sc., F.R.S., will deliver a discourse on that date, on "A Pertinacious Current." Sir Stirling Maxwell being unable to lecture on Thursdays, March 23 and 30, Mr. Thomas G. Jackson, R.A., will deliver two lectures, on the "Reasonableness of Architecture" (illustrated by lantern slides).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, January 18th, 1905.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

MESSRS. T. R. Hodgson, J. K. H. Inglis, J. R. Johnson, and G. F. Phillips were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. James Henry Ashwell, 117, Waterloo Crescent, Nottingham; Samuel Henry Clifford Briggs, B.Sc., Green Bank, Cleckheaton, Yorks.; F. E. Clarke, Ph.D., B.Sc., Pennsylvania State College, Pa., U.S.A.; Charles Richard Gardner, Green Cottage, Brunswick Square, Gloucester; Frederick William Heeley, 10, Yarrowburgh Street, Grimsby; James Alexander Russell Henderson, B.Sc., Chihli Provincial College, Paotingfu, N. China; Percy Walter Jones, Toowong, Brisbane, Queensland; Joseph Lister, B.Sc., 50, Portland Street, Lancaster; Edward William Lucas, 37, Barton Street, Kensington, W.; Frank Lee Pyman, Ph.D., B.Sc., The Oaks, Hitchin, Herts; Fred Scholefield, B.Sc., 9, Lyndhurst Villas, Magdalen Road, Norwich; John Irwin Scott, B.A., Trent College, Long Eaton, Derbyshire; William Dunham Seaton, 40, Argyle Road, Ilford, Essex; William Herbert Simmons, B.Sc., Oakleigh, Stoke Newington Common, N.; Eric H. Weiskopf, Modderfontein, Transvaal.

The PRESIDENT gave notice that an Extraordinary General Meeting will be held in the Society's Rooms on Wednesday, February 8th, 1905, at 5.30 p.m., to consider the proposal of the Council to make alterations in the By-Laws.

The Council has ordered the following letter and report to be printed in the *Journal* and in the *Proceedings* of the Society:—

Government Laboratory,
Clement's Inn Passage, Strand, London, W.C.
December 6th, 1904.

GENTLEMEN,—I beg to hand you the Report of the International Committee on Atomic Weights, 1905, to which I have appended the names of Professors Moissan and Seubert, as desired by them.

Since the Report was signed I have received, in common I presume with other members of the Committee, a communication from a Committee of the German Chemical Society in reference to the adoption of only one table of numbers in which oxygen should be taken as O=16, to the exclusion of a second table in which the values of the atomic weights were based on H=1. On my communicating with the Chairman as to what action should be taken in consequence of the letter from the Berlin Committee I was informed that the report as adopted had already been despatched to Japan, and was actually in print in America. In these circumstances, and as the Sub-Committee had not had any opportunity of taking the communication from the German Committee into consideration, he considered it desirable that the Report, as adopted, should be presented to the various Societies concerned.—I am, Gentlemen, your obedient Servant,

T. E. THORPE.

The Hon. Secretaries, The Chemical Society,
Burlington House, London, W.

(The Report appeared in our last issue—CHEMICAL NEWS, xci., p. 43).

Of the following papers, those marked * were read:—

*1. "Nitrogen Halogen Derivatives of the Sulphonamides." By FREDERICK DANIEL CHATTAWAY.

The nitrogen halogen derivatives of the sulphonamides, which are obtained by the action of hypochlorous acid on the sulphonamides and the alkylsulphonamides, are remarkable for the great ease with which they can be pre-

pared and crystallised, and for their comparative stability. The sulphon dichloroamides all react with alkali hydroxides, forming the corresponding hypochlorite and the salts of the sulphonmonochloroamides. The latter salts, which are well crystallised, and frequently contain water of crystallisation, only slowly undergo further hydrolysis. They have, in all probability, the *iso*-structure.

The sulphon dichloroamides, alkali sulphonmonochloroamides, and sulphonalkylchloroamides easily enter into all the reactions characteristic of nitrogen chlorides, and illustrate exceptionally well the behaviour of the nitrogen halogen linking, as the various types of simple interaction may with these substances be studied uncomplicated by the transformations which so readily occur with unsubstituted acylphenylchloroamides.

Sulphon dibromoamides and sulphonalkylbromoamides are obtained most easily by a method analogous to that by which the corresponding sulphonchloroamides are prepared; that is, by the action of hypobromous acid on the corresponding amides (compare Hoogewerff and van Dorp, *Rec. Trav. Chim.*, 1887, vi., 373; 1889, viii., 173). They resemble the chloroamides in many of their properties, but are not so stable, and have a bright yellow or orange colour. The dibromoamides, which crystallise well, and can be kept for some days unchanged, slowly decompose on longer keeping, bromine being generally liberated. When warmed with solutions of alkali hydroxides, they form salts, one bromine atom being replaced by metal. These salts are beautifully crystalline pale yellow substances, frequently containing water of crystallisation, which is lost at 100°; when more strongly heated, they decompose explosively. As in the salts of the chloroamides, the metal is probably attached to oxygen.

A large number of typical examples of these compounds were described.

*2. "Electrolytic Oxidation of the Aliphatic Aldehydes." By HERBERT DRAKE LAW.

The chief product of oxidation of the lower members of the saturated aliphatic aldehydes is the corresponding organic acid. To a smaller extent, the oxidation proceeds further, carbon dioxide and carbon monoxide being formed, and in the cases of acetaldehyde and propionaldehyde small quantities of saturated hydrocarbons are also produced, $\text{RCOH} + \text{O} \rightarrow \text{RH} + \text{CO}_2$. No corresponding reaction takes place in the cases of formaldehyde and isobutaldehyde.

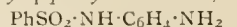
In these experiments, sulphuric acid was used as electrolyte. The gaseous products were collected in Hofmann's electrolytic apparatus fitted with platinum electrodes. The amount of acid formed was estimated in a porous pot fitted with a rotating platinum stirrer.

DISCUSSION.

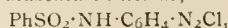
Dr. F. M. PERKIN said that one of the most interesting points brought out in the paper was the formation of small quantities of hydrocarbons in an oxidation process. It was remarkable how extremely stable the aldehydes were to electrolytic oxidation. This was shown most strikingly in the case of the aromatic aldehydes. Thus, if a mixture of toluene and benzaldehyde was subjected to electrolytic oxidation, the hydrocarbon was oxidised in preference to the aldehyde (*Trans. Faraday Soc.*, 1904, 31). Some of the oxidations were best explained by supposing that the hydroxyl group and not free oxygen took part in the reaction, as, for example, in the formation of methyl alcohol in the electrolytic oxidation of an alkali acetate (*Annalen*, 1902, ccxxiii., 304).

*3. "The Diazo-derivatives of the Benzenesulphonyl-phenylenediamines." By GILBERT THOMAS MORGAN and FRANCES MARY GORE MICKLETHWAIT.

Benzenesulphonyl-p-phenylenediamine,—



(m. p. 173°), when diazotised in hydrochloric acid, yields a stable colourless diazonium chloride,—



which, on treatment with aqueous alkalis or sodium acetate,

condenses to form a yellow diazoimide, $C_6H_4 \cdot [N_3] \cdot SO_2Ph$ (m. p. 155°), this substance being produced directly when the base and nitrous acid interact in glacial acetic acid.

The corresponding ortho-compound (m. p. $165-167^\circ$), when treated with nitrous acid either in hydrochloric or glacial acetic acid solution, at once gives rise to a colourless cyclic diazoimide (m. p. 130°); in this case, the intermediate diazonium salt could not be isolated.

When the iminic hydrogen atom of the $PhSO_2 \cdot NH$ group in the foregoing bases is replaced by methyl, the resulting compounds, *benzenesulphonylmethyl-p*- (and *o*-) *phenylenediamines*, yield diazonium salts, $PhSO_2 \cdot NMe \cdot C_6H_4 \cdot N_2Cl$, which do not condense to form diazoimides; these products were characterised by the formation of their azo- β -naphthol derivatives.

Benzenesulphonyl-m-phenylenediamine (m. p. $98-99^\circ$) differs greatly from its ortho- and para-isomerides in its behaviour towards nitrous acid; in hydrochloric acid, it yields a diazonium chloride which, when freed from excess of acid or when treated with aqueous sodium acetate, evolves nitrogen, and becomes converted into an azo-derivative approximating in composition to the formula $PhSO_2 \cdot NH \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(OH) \cdot NH \cdot SO_2Ph$.

This change no longer occurs when the iminic hydrogen is replaced by methyl, and *as-benzenesulphonylmethyl-m-phenylenediamine* (m. p. 96°), like its ortho- and para-isomerides, yields successively a normal diazonium salt and an azo- β -naphthol derivative (m. p. $129-131^\circ$).

DISCUSSION.

Dr. CAIN mentioned that he had diazotised large quantities of *p*-aminoacetanilide in the manufacture of Coomassie Black, but had not noticed the formation of substances analogous to those described by the authors. Their failure to diazotise an amino-group in the ortho-position to a mono-substituted amino-group was in accordance with the work of other investigators on such compounds.

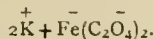
Dr. HEWITT agreed with Dr. Morgan respecting the probably essential difference in structure of the compounds obtained by the action of nitrous acid on the monobenzenesulphonyl derivatives of *o*- and *p*-phenylenediamines. Of the two cyclic formulæ proposed for the ortho-compound, that in which a quinquivalent nitrogen atom was assumed, seemed, however, very improbable; nitrogen, as far as we know, only becoming quinquivalent in the case of salt formation.

Dr. MORGAN, in reply, said that as benzenesulphonyl-*p*-phenylenediamine had been found to yield a new type of diazoimide, it became of interest to ascertain the behaviour of the similarly substituted ortho- and meta-diamines under comparable conditions.

With reference to the alternative diazonium formula for the ortho-diazoimide, it seemed necessary to consider this possible configuration, inasmuch as, on account of the distinctly acidic nature of the complex $C_6H_5 \cdot SO_2 \cdot NH$, the condensation of this substituent with the adjacent basic diazonium group might be regarded as involving the formation of an internal salt.

*4. "The Molecular Condition in Solution of Ferrous Potassium Oxalate." By SAMUEL EDWARD SHEPPARD and CHARLES EDWARD KENNETH MEES.

Ferrous oxalate dissolves in alkali oxalates, forming double salts, such as $K_2Fe(C_2O_4)_2$, which dissociate according to the scheme—



The complex anion, $Fe(C_2O_4)_2^-$, is not very stable, and by solubility determinations the value 0.8 was found for the constant—

$$K = \frac{Fe(C_2O_4)_2^-}{C_{Fe} \cdot C_{C_2O_4}^2}$$

at 20° .

Spectrophotometric measurements showed that the formation of ferrous ions at moderate dilutions was negligibly small.

The action of acids is to precipitate ferrous oxalate by removing free oxalate ions, thus disturbing the equilibrium indicated above.

The absorption-spectrum was measured at three concentrations. The absorption is unilateral, increasing uniformly toward the violet end of the spectrum.

*5. "A Further Analogy between the Asymmetric Nitrogen and Carbon Atoms." By HUMPHREY OWEN JONES.

In the present state of our knowledge of the stereoisomerism of quinquivalent nitrogen compounds, any definite knowledge about the similarity and difference between them and asymmetric carbon compounds is of value. The author has proved that, during the formation of an asymmetric nitrogen atom in a compound containing an asymmetric carbon atom, two isomerides, which are called the α - and β -compounds, are produced. Methyl-*l*-amylaniline has been combined with allyl and benzyl iodides.

The dextrorotatory α -allyl compound can be isolated by crystallisation from alcohol; ($[\alpha]_D$ in chloroform = 21.8° , gradually falling to 3.1° as the α -isomeride changes into the β -derivative until equilibrium is attained.

The two benzyl compounds cannot be separated in the same way, because the difference in solubility is not great, and they are very labile. They have therefore been separated by means of their camphorsulphonates. α -Phenylbenzylmethyl-*l*-amylammonium iodide melts at $144-145^\circ$ and has ($[\alpha]_D$ in chloroform = 65°); the β -compound melts at $131-132^\circ$, and has ($[\alpha]_D$ = -18.8°).

The chloroform solutions of both compounds change rapidly until equilibrium is attained with ($[\alpha]_D$ = 2.8°).

6. "The Formation of Magnesia from Magnesium Carbonate by Heat and the Effect of Temperature on the Properties of the Product." By WILLIAM CARRICK ANDERSON.

Magnesia prepared from different substances and by different methods is known to vary greatly in properties, and it is generally supposed that this is due either to variation in the size of the molecule of the oxide, or to a difference in the grouping of the magnesium and oxygen atoms in the molecule, or to both of these causes. In the absence of a method of determining the molecular weights of solid substances, evidence in support of the view that the magnesia is polymerised must be indirect.

Experiments were conducted on the native magnesium carbonate (magnesite) and on three forms of artificial carbonate, with the view of ascertaining (1) the lowest temperature at which the evolution of carbon dioxide could be distinctly recognised; (2) the comparative rates at which the expulsion of the gas takes place at higher temperatures under atmospheric pressure; and (3) the extent to which the samples of magnesia thus obtained dissolve in water after being kept at different known temperatures for a fixed period. This solubility was determined after leaving an excess of the specimen in water for two hours at 20° .

In twenty hours at 350° , native magnesite yielded a quantity of carbon dioxide equal to 0.40 per cent of its weight, and the rate of evolution increased rapidly with rise of temperature. Complete expulsion was reached at about 750° with two at least of the artificial carbonates, but only above 810° in the case of the third ("heavy carbonate").

The rate of solution of the magnesia obtained by heating the "heavy carbonate" was found to be greater than that of the samples obtained from "light" and "crystal" carbonate under the same conditions, so long as the heating was little more than that needed for complete decomposition of the carbonates. As the temperatures of preparation were increased, the rate of solution diminished in every instance, but much more rapidly in the case of the "heavy" oxide than in those of the other two.

It is inferred from these results that polymerisation takes place when magnesia is heated, and that this goes on

faster in the dense "heavy" oxide than in the lighter specimens of magnesia. The rate of solution as determined in the experiments is believed to be a measure of the rate of hydration, and this appears to be most rapid in the molecule $(\text{MgO})_n$ obtained by heating the heavy carbonate at 810° .

7. "Transformations of Derivatives of *s*-Tribromodiazobenzene." By KENNEDY JOSEPH PREVITÉ ORTON.

The discrepancy between the results obtained by the author (*Proc. Roy. Soc.*, 1902, lxxi., 153; *Trans.*, 1903, lxxxiii., 796), and by Hantzsch (*Hantzsch and Pohl. Ber.*, 1902, xxxv., 2964; and *Hantzsch, Ber.*, 1903, xxxvi., 2069), with respect to the transformations of *s*-tribromobenzenediazonium salts and *s*-tribromobenzenediazotates, has led the author to re-investigate these reactions.

According to the author, in solutions of the diazonium salts of weak acids, that is, solutions in which the ions $(\text{C}_6\text{H}_2\text{Br}_3\text{N}_2)^+$ and $(\text{OH})^-$ are simultaneously present, a replacement of a bromine atom by hydroxyl takes place, bromine ions appearing in the solution, and 3:5-dibromo-*o*-benzoquinonediazide ($3:5$ -dibromodiazophenol), $\text{O}:\text{C}_6\text{H}_2\text{Br}_2\text{N}_2$, being formed. A similar decomposition takes place when a solution of the corresponding *s*-tribromobenzenediazotate is treated with quantities of an acid insufficient to convert the diazo-compound into the diazonium salt, the free diazohydroxide, $\text{C}_6\text{H}_2\text{Br}_3\text{N}:\text{N}:\text{OH}$, thus formed, probably now cleaving into the groups $(\text{C}_6\text{H}_2\text{Br}_3\text{N}_2)^+$ and $(\text{OH})^-$.

According to Hantzsch, on the other hand, under both conditions the primary product of the change is *s*-tribromophenylnitrosoamine, $\text{C}_6\text{H}_2\text{Br}_3\text{N}:\text{NH}:\text{NO}$, a substance which, although at first thought to be readily capable of isolation (*Ber.*, 1902, xxxv., 2964), is now stated (*Ber.*, 1903, xxxvi., 2069) to be unstable, and at any but low temperatures, liable to decompose into the quinonediazide with the elimination of hydrogen bromide.

The difference between these two results is ascribed by Hantzsch to the fact that the author carried out his experiments at the ordinary temperature, and not at as low a temperature as possible.

In the new experiments, the solutions have been kept partially frozen during the reaction, and the primary product has been examined in order to ascertain if any decomposition, which was accompanied by the formation of quinonediazide and the elimination of hydrogen bromide, could be detected. The author's earlier observations, namely, that the primary product was a mixture of a complex condensation product with the quinonediazide, were completely confirmed.

The proportion of the quinonediazide in the primary yellow product was estimated by conversion into the azo- β -naphthol derivative, and found to represent about 12 per cent of the diazonium hydrogen sulphate, when 2 gramm.-mols. of hydrogen carbonate were used for each gramm.-mol. of diazonium salt; at the same time it was shown that the quinonediazide did not arise during the operation from the decomposition of *s*-tribromophenylnitrosoamine, as no simultaneous formation of hydrogen bromide could be detected.

In the yellow aqueous extract of the primary product, which, according to Hantzsch, contains the nitrosoamine in solution, the author was unable to find any substance but the quinonediazide. On keeping or on heating, no decomposition accompanied by the elimination of hydrogen bromide was observed; the diazophenol could be completely extracted from the solution by chloroform, and then coupled with alcoholic β -naphthol; lastly, when exposed to light, the solution behaved in the manner characteristic of diazophenols.

Experiments showed that between the limits of 0° and 15° temperature has but little effect on the extent of the decomposition of the *s*-tribromodiazobenzene; as the author has previously stated, the prime factors appear to be the concentrations of the ions $(\text{C}_6\text{H}_2\text{Br}_3\text{N}_2)^+$ and $(\text{OH})^-$.

The author sees, therefore, no reason for modifying the

views expressed by him in former papers as to the mechanism of this reaction, and thinks that at present there is not sufficient evidence for supposing that a nitrosoamine is the primary product, which subsequently decomposes into quinonediazide and hydrogen bromide.

8. "The Addition of Sodium Hydrogen Sulphite to Ketonic Compounds." By ALFRED WALTER STEWART.

The statement made by Beilstein in his *Handbuch* (3rd ed., I., 999), that pinacolone forms no addition product with sodium hydrogen sulphite, when taken in conjunction with the current idea that "bisulphite" compounds are formed only with those ketones which contain the acetyl group, suggests that the introduction of methyl groups into the ketonic chain has a tendency to prevent the formation of an additive product. With the view of testing the correctness of this idea, and in order to estimate the relative amounts of the double compounds formed with different ketones, advantage was taken of the fact that iodine solution does not oxidise the SO_3Na group of a ketonic bisulphite compound. Thus, if two solutions, one of pure sodium hydrogen sulphite and the other containing a mixture of this salt and a ketonic compound, are titrated, the difference in the number obtained on titration indicates the amount of additive product formed. This method was applied to several compounds containing the acetyl group, and the principal results are shown in the following table:—

	Percentage of bisulphite compound formed in—			
	10 mins.	30 mins.	50 mins.	70 mins.
Acetaldehyde	85.0	88.0	88.7	88.7
Acetone	28.5	47.0	55.9	58.9
Methyl ethyl ketone . .	14.5	25.1	32.4	38.4
Methyl propyl ketone . .	8.5	14.8	19.6	25.5
Methyl isopropyl ketone	4.2	7.5	11.6	13.0
Pinacolone	4.2	5.6	5.6	5.6

9. "The Reduction Products of Anisic Acid." By JOHN SCOTT LUMSDEN.

When anisic acid dissolved in amyl alcohol is reduced by sodium, the products of reduction are hexahydrobenzoic acid and δ -keto-hexahydrobenzoic acid. The formation of the former acid is explained by the removal of the methoxy-group of anisic acid and the complete hydrogenation of the ring, but the production of the δ -ketonic acid is more difficult to understand, being probably due to four hydrogen atoms becoming attached, and then, by the agency of one molecule of water, the methyl group is removed as methyl alcohol, and the hydrogen of the water is added to the γ -carbon atom. By analysis of the ketonic acid and its salts, and from the melting point of the semicarbazone, it is proved to be identical with the acid recently prepared synthetically by Perkin (*Trans.*, 1904, lxxxv., 416).

10. "The Physical Properties of Heptoic, Hexahydrobenzoic, and Benzoic Acids and their Derivatives." By JOHN SCOTT LUMSDEN.

From hexahydrobenzoic acid, which was obtained pure from anisic acid, the methyl, ethyl, and propyl esters, the acid chloride and anhydride, and the amide and anilide were prepared and their properties compared with the corresponding compounds of heptoic and benzoic acids. It was found that the properties of hexahydrobenzoic acid and its derivatives were in general intermediate between those of the other two acids, the melting points, boiling points, specific gravities, and refractive indices being higher than those of the heptoic, and lower than those of the benzoic acid series.

The solubilities of the three acids are nearly alike, but the affinity constant of the hexahydro-acid is lower than that of benzoic acid, and is like the value of that of an acid of the fatty series. The boiling-points of the hexahydro-compounds are regularly 9° higher than the heptoic, and 15° lower than the corresponding benzoic derivatives. A comparison of the molecular volumes showed that a hexamethylene ring and a benzene nucleus have identical

volumes, while measurements with a Pulfrich's refractometer proved that the hexamethylene structure has no influence on the refraction of light, but that a benzene nucleus retards light to an amount equal to that due to six hydrogen atoms, thus making the molecular refractions of the corresponding derivatives of benzoic and hexahydrobenzoic acid identical.

II. "The Influence of Solvents on the Rotation of Optically Active Compounds. Part VII. Solution-volume and Rotation of Menthyl and Menthyl Tartrates." By THOMAS STEWART PATTERSON and FRANCIS TAYLOR.

The authors have examined the rotation of menthyl, *l*-menthyl, *d*-tartrate, and *l*-menthyl diacetyl-*d*-tartrate in ethyl alcohol, benzene, and nitrobenzene, and have compared the values obtained with the corresponding values for molecular-solution-volume. The results were considered, on the whole, to confirm the suggestion that rotation in solution and molecular-solution-volume are closely related phenomena. For menthyl, the facts are in complete agreement with theory. With menthyl tartrate, the results for alcohol and nitrobenzene are in good agreement, although the relationship between the two variables in benzene is anomalous. Difficulties are met with also for menthyl diacetyl-tartrate; but although in alcohol and benzene the relationship is not a quantitative one, it is in accordance with theory in so far as, in both cases, contraction brings about increased rotation. Out of the nine examples studied, seven are in agreement with the relationship suggested.

NOTICES OF BOOKS.

Heat. By J. H. POYNTING, Sc.D., F.R.S., and J. J. THOMSON, M.A., F.R.S., Hon. Sc.D., Dublin. London: Charles Griffin and Co., Ltd. 1904.

This volume is the third of a series forming a complete text-book of physics. While the practical applications of the principles involved are emphasised, the theoretical side is by no means neglected, and, indeed, the authors are most successful in their treatment of the kinetic theory of matter and thermodynamics, though they have somewhat handicapped themselves by reducing the use of mathematical methods to the very minimum. This does not, of course, mean to imply that the student is supposed to be unfamiliar with the use of the calculi, but his knowledge need not extend beyond their elements. The chapters on thermodynamics are most characteristically written, and in them is included some matter which is not generally to be found in such treatises, but is none the less useful from the student's point of view. The subject of heat is certainly one which specially lends itself to the treatment the authors have given it, and is perhaps one of the easiest branches of physics in which to give the student thoroughly comprehensive and fundamental notions, and this text-book can be recommended as containing all that is required up to the standard of the ordinary science degree of the University of London, and similar examinations.

The Study of Chemical Composition. By IDA FREUND. Cambridge: The University Press. 1904.

THIS book aims at tracing the historical development of theories regarding chemical composition, the ultimate constitution of matter, and the genesis of the elements from the earliest times to the present day. The quotations, of which it largely consists, are excellently chosen from papers which in most cases may be regarded as classical, and the connecting explanations are brightly and clearly written; one very salient feature of the book is the abundance of summaries and abstracts, which simplify the subject for the student, and show very strikingly the value of method in scientific work. The student who has not the

time or opportunity to refer to original papers is given excellent abstracts of, and sufficiently full quotations from them, to enable him to get at the gist of the matter, and will find himself materially aided by the able and methodical explanatory connecting links, on such subjects as theories of combustion or the development of the laws of chemical constitution, and the parts played by the various investigators are judiciously estimated at their true worth. The reading of such a book can hardly fail to inspire a keen and genuine enthusiasm for the subject, such as evidently animated the authoress in the writing, and no single page in it is dull or wearisome in the least degree. The inclusion of what practically amounts to a short dissertation on crystalline form hardly seems warranted by the reasons given for it, for it is only such as is to be found in almost any text-book of inorganic chemistry.

A Text book of Physiological Chemistry. By OLOF HAMMARSTEN. Authorised Translation by JOHN A. MANDEL, Sc.D. Fourth Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1904.

THE translation of this useful text-book of physiological chemistry is probably too well known to students to require any further recommendation. There seems little likelihood of its being displaced by any other text-book of similar scope, and it will no doubt for some time to come be regarded as practically indispensable by physiologists. This American edition has been prepared from the fifth German edition, which the author has revised and brought up-to-date, so that the most recent discoveries and suggestions of facts and theories are to be found fully discussed in it.

A Handbook of Chemical Engineering By GEORGE E. DAVIS. Second Edition. Manchester: Davis Bros. 1904.

IN the second edition of this handbook many improvements and additions have been made, the most important of which are perhaps those dealing with the use of the electromagnetic separator, and with the application of heat and cold. It is noticeable that in the latter chapter the subject of liquid fuel is accorded very little space, and recent valuable additions to literature bearing upon it, the study of which would possibly tend to cause the author to modify his views somewhat, are altogether ignored. Numerous practical examples have now been introduced for the first time; for instance, on stresses on beams, wind pressure on vitriol towers, cost of moving gases, &c., and we are glad to see that the number of working drawings is also greatly increased, those included in the first edition being quite inadequate; even now for practical purposes many of the illustrations of complicated machinery might advantageously be replaced by sectional drawings.

Announcement.—The copyright of that most useful and popular hand-book, "Half-hours with the Microscope," by Dr. Edwin Lankester, formerly published by Messrs. W. H. Allen and Co., has been acquired by Messrs. C. Arthur Pearson, Ltd., who have also purchased the companion volume by Thomas Davies, on the "Preparation and Mounting of Microscopic Objects." The latter has been out of print for some time, but a new and cheaper edition will be published very shortly.

Thermo-electricity of Aluminium Alloys.—Hector Pecheux.—The author examines various aluminium alloys, and finds that $ZnAl_6$ and $ZnAl_{10}$ are the ones having the highest thermo-electric power with regard to copper above 180° . $ZnAl_6$ is at first below the other values, but approaches them towards 380° .—*Comptes Rendus*, CXXXIX., No. 26.

CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxi., No. 1, January 2, 1905.

Influence of Water Vapour on the Reduction of Iron Oxides by Carbonic Oxide and Carbonic Anhydride.—O. Boudouard.—The author's experiments show that reducing gases when in a dry state have a more energetic action than when wet. The difference, which is considerable at low temperatures, becomes imperceptible at about 1000°. The phenomenon presents exactly the same aspect whether equal volumes of CO and CO₂ act on sesquioxide of iron, or whether carbonic oxide acts on iron protoxide. In the regions of lower temperatures of furnaces, with dry gases, the reduction of iron oxide by carbonic oxide is more complete. It is known that the reaction of the carbonic acid thus formed on the carbon is less energetic as the temperature is lowered, and there finally results an economy of fuel. It is necessary, however, to point out that, in high-temperature furnaces, near the tuyères the water vapour is decomposed into hydrogen and oxygen, and there are no actual constants as to the final effect of the hydrogen which, in presence of carbon dioxide, can regenerate water vapour and carbon monoxide.

Existence of a Green Sulphate of Chromium Sesquioxide.—Albert Colson.—A cryoscopic and chemical investigation shows that the chromium sulphate resulting from the reduction of chromic acid by sulphurous acid gas contains three sulphuric radicles (3SO₄). Further, this salt, Cr₂(SO₄)₃·10H₂O, is a green normal sulphate, in every way comparable with the corresponding violet salt. The author has finally given to this substance an accurate constitutional formula,

$$\text{SO}_4 \begin{array}{c} \diagup \quad \diagdown \\ \text{Cr} \quad \text{Cr} \\ \diagdown \quad \diagup \\ \text{SO}_4 \end{array} \text{SO}_4$$
 He still has to discover whether there exists a radicle common to the isomeric green salts, and also to obtain other salts corresponding to this sulphate.

Separation of the Three Dimethylantracenes obtained from the Action of Methylene Chloride and Aluminium Chloride on Toluene.—James Lavaux.—In a previous paper the author enumerated the new bodies which he isolated amongst the products of the reaction of CH₂Cl₂ on toluene in presence of AlCl₃. He now gives an account of the various modifications which he has introduced into Friedel and Craft's method of operation, and the methods employed in order to separate the three dimethylantracenes produced by the reaction.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxvii., No. 18, 1904.

Action of Benzyl Magnesium Chloride on Crystal Violet.—Martin Freund and Heinrich Beck.—A solution of benzyl magnesium chloride containing 10.2 grms. benzyl chloride and 2 grms. magnesium in 100 c.c. absolute ether was added to 8 grms. pure crystal violet, dried at 115°–120°. The mixture was digested for some hours with a reflux condenser. The dye thus became transformed first into a brown and then a grey powder. Water was added in a separating funnel, when the liquid became bluish violet, due to the unchanged crystal violet. Concentrated hydrochloric acid was then added, and the acid solution separated from the ether and saturated with ammonia, when a bluish substance was precipitated. On addition of alcohol to this, the liquid acquired an intense violet colour, the substance remaining undissolved, but becoming of a lighter colour. By repeatedly heating with alcohol, the substance could be separated from the

colouring matter, but it always became blue again in air. It was very soluble in chloroform, and crystallised from it on addition of absolute alcohol in fine needles uniting to form spherical aggregates. The composition of these crystals is represented by the formula C₃₂H₃₇N₃.

Triamine Cobalt Salts, and a New Case of Hydrate Isomerism.—A. Werner and Ad. Grün.—By filtering a freshly prepared solution of chlorodiaquo-triamine cobalt chloride into cooled nitric acid or hydrobromic acid, the corresponding nitrate or bromide is formed. They both form violet crystals which give a blue solution in water. Their existence in the solid state is of only very short duration; thus the bromide on being kept in the desiccator loses a molecule of water, and forms a green salt

$$\left[\begin{array}{c} \text{Cl} \quad (\text{OH})_2 \\ \text{Br} \quad \text{Co} \quad (\text{NH}_3)_3 \end{array} \right] \text{Br}$$
 and when an attempt is made to precipitate it from its aqueous solution with hydrobromic acid, a brown salt is obtained, of the same composition as the original bromide, but having quite different properties. The green bromide mentioned above changes into this same brown salt on standing in moist air. The brown and blue bromides are isomeric, and both are simple triamine salts. Thus the isomerism must be a case of stereo-isomerism, or else must be due to the different method of combination of the water molecule. It can be easily shown that the latter supposition is correct. While from the blue bromide, with sulphuric acid, the corresponding sulphate of formula

$$\left[\begin{array}{c} \text{Cl} \quad (\text{OH})_2 \\ \text{Br} \quad \text{Co} \quad (\text{NH}_3)_3 \end{array} \right] \text{SO}_4$$
 results, from the brown and green bromides a compound is formed, which shows by its green colour, that it belongs to the diacido salts, and is a sulphate of the chlorobromo-aquo-triamine cobalt series. Hence, in both the brown and green salts there must be a radicle

$$\left[\begin{array}{c} \text{Cl} \quad (\text{OH})_2 \\ \text{Br} \quad \text{Co} \quad (\text{NH}_3)_3 \end{array} \right]^+$$
 and thus one molecule of water in the brown salt cannot be combined intra-radically. Thus the brown salt must have the following composition

$$\left[\begin{array}{c} \text{Cl} \quad (\text{OH})_2 \\ \text{Br} \quad \text{Co} \quad (\text{NH}_3)_3 \end{array} \right] \text{Br} + 1 \text{ aq.}$$
 The blue bromide is isomeric with the brown, the former being represented by the formula

$$\left[\begin{array}{c} \text{Cl} \quad (\text{OH})_2 \\ \text{Cl} \quad \text{Co} \quad (\text{NH}_3)_3 \end{array} \right] \text{Br}_2$$
 and the latter by

$$\left[\begin{array}{c} \text{Br} \\ \text{Cl} \quad \text{Co} \quad (\text{OH})_2 \\ \quad \quad (\text{NH}_3)_3 \end{array} \right] \text{Br} + 1 \text{ aq.},$$
 and both of them give the compound

$$\left[\begin{array}{c} \text{Cl} \quad (\text{OH})_2 \\ \text{Br} \quad \text{Co} \quad (\text{NH}_3)_3 \end{array} \right] \text{Br}$$
 losing

one molecule of water. The extra radical molecule of water in the brown isomer, which is not given up in the desiccator, is much more firmly bound than the H₂O in the blue bromide, which is directly combined with the cobalt. The extra radical H₂O in the brown bromide is given up at 100°. Thus, in determinations of the constitution of aqueous hydrate compounds it must be noted that the fact that one H₂O is more readily given up, does not prove that this molecule of water does not belong to the complex radicle.

Ullmann and Borsum's so-called "Hexaphenylethane," and the Trivalency of Carbon.—A. E. Tschitschibabin.—The simplest explanation of the properties of Gomberg's triphenylmethyl is the supposition that they are due to the formation of the saturated hydrocarbon hexaphenylethane. The reasons in favour of this assumption are as follows:—1. It is a well-known fact that the substances which contain many electro-negative radicles or atoms are inclined to split up at those places in the molecule at which the accumulation of such radicles exists. 2. Peculiarities of structure sometimes force substances with single bonds to behave like unsaturated bodies. 3. Many substances react with the oxygen of the air, even at ordinary temperatures, frequently giving rise to peroxide compounds as the first products. Saturated substances also possess this power more or less, and it is probable that the power of autoxidation is more widely spread

among organic substances than is generally supposed. 4. Finally, Gomberg has shown that the undoubtedly saturated substance of allied structure triphenyliodo-methane, when dissolved, absorbs oxygen with the same ease as triphenylmethyl itself, giving rise to the same oxidation product, similar to a peroxide. Gomberg has now found that the molecular weight of his triphenyl-methyl is double that corresponding to the formula, but the supposition that it forms hexaphenylethane is contradicted by the fact that another stable hydrocarbon, different from hexaphenylethane, has this composition. Peculiarities in the formation and properties of Ullmann and Borsum's hydrocarbon led the author to ascribe to it a different structure. 1. The hydrocarbon is more stable towards oxidising agents than hexaphenylethane would be expected to be. 2. The formation of hexaphenylethane takes place under anomalous conditions, in that the presence of a condensation agent is essential. Hence, this leads to the supposition that a condensation takes place between the triphenylcarbinol and the triphenylmethane, leading to the formation of a derivative of tetraphenylmethane,—

$$(C_6H_5)_3C.OH + C_6H_5.CH(C_6H_5)_2 =$$

$$= (C_6H_5)_3C.C_6H_4.CH(C_6H_5)_2 + H_2O.$$

Finally, it must be remembered that the triphenylmethane derivatives are not always easily oxidised to the corresponding carbinols. This formula is confirmed by the fact that in sunlight a solution of the substance in CS_2 reacts very easily with bromine, only one Br molecule reacting. Thus practically quantitatively a monobromide is formed, with properties exactly similar to those of triphenylbrom-methane. This very readily gives up its bromine at the ordinary temperatures, when treated with alcohol, water, or acetic acid. In water, in the presence of pyridine, the bromine splits off quantitatively, and the carbinol $(C_6H_5)_3C.C_6H_4.C(OH)(C_6H_5)_2$ is formed. The above facts show that Ullmann and Borsum's compound is not hexaphenylethane, but possesses the above structure. Gomberg's assumption that his hydrocarbon has, under certain conditions, a molecular weight corresponding to that of triphenylmethyl, has not been confirmed.

Volumetric Determination of Hydroxylamine by means of Trivalent Titanium.—Arthur Stähler.—21 c.c. of a solution of 4 grms. of hydroxylamine sulphate in 1000 c.c. water were diluted with about 80 c.c. of boiling water, and titanium solution containing 0.004258 gm. Ti⁺⁺⁺ per c.c. was added in excess, carbon dioxide being simultaneously introduced into the vessel. The unused trivalent titanium was titrated back with n/10 permanganate. The reaction proceeds as follows:—

$$Ti_2O_3 + NH_3O = 2TiO_2 + NH_3.$$
The same method can be used for the determination of organic hydroxylamine substances. Hydrazine sulphate, however, is not affected by titanium trichloride under these conditions.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxxi., No. 7.

Electrolysis with an Alternating Current.—André Brochet and Joseph Petit.—Already noticed.

New Syntheses effected by Means of Molecules containing the Methylene Group Associated with One or Two Negative Radicals. 1. Action of Epichlorhydrine and Epibromhydrine on the Benzoyl-acetic Soda Ethers, and on Cyano-soda Camphor.—A. Haller.—Already noticed.

A New Aromatic Hydrocarbide "Phenylace-naphthylmethane."—Charles Dziewonski and Eligio Dotta.—The group of new hydrocarbides obtained by the action of chloride of benzyl on the aromatic hydrocarbides are of a general type, $C_6H_5CH_2\bar{R}$, in which R represents an aromatic radical combined with the benzyl or the

phenylmethene ($C_6H_5CH_2-$) group. Among the most interesting syntheses of this nature are those of α - and β -phenylnaphthylmethane. This hydrocarbide is formed, as a rule, by the action of chloride of benzyl on acenaphthene in the presence of zinc powder or chloride of zinc. After the first reaction, the details of which are fully described, the mass is heated further for two hours, raising the temperature to 160–180°; the still warm liquid is decanted into a retort and distilled, the fractions being separated as described. The portion passing at 320–330° is collected and submitted to a further fractional distillation. In this manner we obtain a liquid distilling at 335–350°, consisting of nearly pure phenylacenaphthylmethane; this is crystal-lised several times in boiling alcohol, and forms long white silky needles. It is easily soluble in boiling alcohol, ether, benzene, &c., as well as in cold sulphuric acid, which it colours yellow; it fuses at 112–113°, and boils at 340–345°. With a large excess of picric acid this substance gives a reddish compound, not easy to purify, as it decomposes as soon as it is washed with the smallest quantity of any solvent. Analysis gives the empirical formula $C_{19}H_{16}$ for the hydrocarbide.

Some Derivatives of α -Campholytic Racemic Acid, and of α -Campholenic Racemic Acid.—G. Blanc and M. Desfontaines.—Already noticed.

The Action of Bromine on Strychnine.—Leon Martin.—The examination of the action of bromine on strychnine has enabled the author to obtain a series of derivatives with well-defined properties. A number of these bodies are described by the author, among them being monobromostychnine, iodomethylate of monobromostychnine, bibromostychnine, &c. Iodine also acts on strychnine, giving three kinds of derivatives, according to whether it is substituted for the hydrogen in the molecule, united with the hydrogen in the form of a haloid salt, or fixed in the so-called state of addition, similar to water of crystallisation.

Method for the Estimation of Prussian Blue.—Ch. Coffignier.—Already inserted in full.

New Method for the Estimation of Halogen Bodies in Organic Compounds. Chlorine and Bromine.—H. Baubigny and G. Chavanne.—Already noticed.

The Formation of Terpenic Compounds in Chloro-phyllian Organism.—Eug. Charabot and Alex. Hebert.

Does Free Glycerin Exist in Normal Blood?—A. Mouneyrat.—The result of the author's research on this subject leaves him with the opinion that the existence, or not, of glycerin in normal blood is undecided.

MEETINGS FOR THE WEEK.

- MONDAY, 6th.—Society of Arts, 8. (Cantor Lecture), "Reservoir Stylographic, and Fountain Pens," by James P. Maginot, Assoc. M Inst. C.E., &c.
 — Society of Chemical Industry, 8. "The Theory of Dyeing—Part II., Pseudo-solution and Desolution," by W. P. Dreyer. "The Fading of Inks and Pigments" by J. W. Lovibond.
 — Royal Institution, 5. General Monthly Meeting.
 TUESDAY, 7th.—Royal Institution, 5. "The Structure and Life of Animals," by Prof. L. C. Miall, D.Sc., F.R.S.
 WEDNESDAY, 8th.—Society of Arts, 8. "Time Development in Photography, and Modern Mechanical Methods of carrying it out," by R. Child Bayley.
 THURSDAY, 9th.—Royal Institution, 5. "Forestry in the British Empire," by Prof. W. Schlich, F.R.S., &c.
 FRIDAY, 10th.—Royal Institution, 9. "Art of the Ionian Greeks," by Cecil Smith, LL.D.
 — Physical, 8. The President-Elect, Prof J. H. Poynting, will deliver an Address on "Radiation Pressure."
 SATURDAY, 12th.—Royal Institution, 3. "The Bohemian School of Music" (with Musical Illustrations), by Sir Alexander Mackenzie, Mus. Doc., D.C.L., LL.D.

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THE CHEMICAL NEWS.

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ON THE

ULTRA-VIOLET SPECTRUM OF GADOLINIUM.*

By Sir WILLIAM CROOKES, D.Sc., F.R.S.†

GADOLINIUM oxide is a rare earth, occurring between yttrium and samarium. It was discovered in 1880 by Marignac, and was at first called by him Ya, a designation which he soon changed for gadolinium. Since Marignac's time much work has been done on this earth by Lecoq de Boisbaudran, Bettendorf, Cleve, Benedicks, Marc, Demarcay, Exner and Haschek, Urbain, and others.

In the spring of this year, M. G. Urbain gave me some gadolinia and other rare earths, which he had prepared in a state of considerable purity by means of a novel system of fractionation in which use is made of the crystallisation of double nitrates of bismuth and magnesium with the rare earth nitrates. He finds that bismuth places itself between the ceric and the terbic groups, thus sharply separating samarium, the last member of the ceric group, from europium and gadolinium, the first members of the terbic groups. I have for some time past been fractionating rare earths by Urbain's method, and can quite corroborate what he says.

The ultra-violet spectrum of gadolinium has been measured by Exner and Haschek, who have published their results in a book, "Wellenlängen-Tabellen für Spektralanalytische Untersuchungen" (F. Deuticke, Leipzig and Wien, 1902). These observers used a material prepared by Dr. L. Haitinger, in which they say holmium, samarium, and yttrium were present as impurities. They give wave-lengths of 1150 lines; I have found them to be as a rule very accurate, and in the maps accompanying this I have adopted most of their wave-lengths, except in cases where my own measurements give different figures, or where lines given by them are not to be distinguished on my photographs. In some cases also lines ascribed to gadolinium appear to be caused by other earths as impurities.

My photographs were taken by means of the apparatus described in my paper "On the Ultra-Violet Spectrum of Radium" (*Proc. Roy. Soc.*, August, 1903, vol. lxxii., p. 295; and *CHEMICAL NEWS*, 1903, vol. lxxxviii., p. 202). The arrangement is the same as there adopted in the maps of the radium spectrum. The upper half of each strip shows the iron lines used as standards, with their wave-lengths according to Rowland's latest measurements. The lower half contains the gadolinium lines, with their wave-lengths re-calculated or verified from the iron standards, according to the method given in detail in the paper just quoted. Other lines, the wave-lengths of which are written in red ink, are either platinum lines or lines due to traces of impurity in the gadolinium oxide. These are very few, and their faintness speaks well for the accuracy with which M. Urbain has separated other earths from the gadolinium, for in my experience I have seldom found a so-called "pure" salt of an ordinary metal anything like so free from impurities as this earth proves to be. Moreover, it must not be taken as certain that some of the impurities assumed to be present on the strength of a strong line are really there, because in some instances I have not been able to detect the presence of another equally characteristic line of the same impurity.

The rare elements allied to gadolinium, or occurring with it, which I have thus found to be present, are:—

Yttrium, represented by the lines at	3774.51 and 4177.68
Europium " " "	3972.16, 4129.90, and 4662.08
Samarium " " "	3230.65
Ytterbium " " "	3289.52 and 3694.35
Scandium " " "	3572.71, 3613.96, and 3630.86

The other elements which are present are:—

Bismuth, represented by the line at	4259.85
Magnesium " " lines at	2796.62 and 2802.80
Calcium " " "	3933.81 and 3968.60

Of these, the bismuth and magnesium are present from the salts used in the fractionation,* while calcium is represented by the great H and K pair, which are almost always present in earthy spectra.

I have also examined the phosphorescent spectrum of Urbain's gadolinium by means of photography. In 1886, I communicated a paper to the Royal Society (*Proc. Roy. Soc.*, Feb., 1886, vol. xl., p. 236; and *CHEMICAL NEWS*, 1886, vol. liii., p. 133), on the visible spectrum of phosphorescing Ya (gadolinia), given to me by Marignac, and also prepared by myself, and later in the year (*Proc. Roy. Soc.*, June, 1886, vol. xl., p. 503), I said that the gadolinium I was then working with showed, on the evidence of its phosphorescent spectrum, the presence of samarium and other impurities. Since that time I have used the photographic method of examining phosphorescent spectra, and in 1899 I brought before the Royal Society (*Proc. Roy. Soc.*, May, 1899, vol. lxxix., p. 237; and *CHEMICAL NEWS*, 1899, vol. lxxix., p. 212), a preliminary notice of a new element, Victorium, the existence of which I was led to infer from its chemical properties, and from some bands in its phosphorescent spectrum. These bands consist of a strong group high up in the ultra-violet spectrum, having wave-lengths of 3117—3120, 3060, 3064, and 3219.

The specimens of gadolinia prepared by myself in 1886, as well as that sent me by Marignac, gave these victorium bands faintly, and the gadolinia given me by M. Urbain also showed the same bands in greater strength than the other lines and bands I have ascribed to samarium and yttrium. Early this month M. Urbain has sent me a specimen of gadolinium which he considers quite pure, and on testing it in the vacuum tube for its phosphorescent spectrum I find the victorium bands photograph stronger than they came out in the other specimen. At the same time I do not think that victorium is gadolinium. All the evidence from chemical and phosphorescent data tends to the conclusion that victorium is only present as an impurity in the gadolinium, and the strength with which it reveals its presence is mainly due to the excessive delicacy of the test.

Micrographic Examination of the Meteorite found in Cañon Diablo.—H. Moissan and F. Osmond.—A micrographic investigation of the meteorite recently found in Cañon Diablo shows that the metallic portions, which appear to be homogeneous, often contain microscopic nodules and irregularities, consisting of superposed layers of iron phosphide and carbide. A further examination of those nodules which have not been subject to external oxidation shows them to be formed of iron sulphide, or troilite, surrounded by successive layers of iron phosphide and carbide. On examining further nodules, the authors conclude that this sulphide has apparently already been subjected to the phenomena of oxidation, and in certain cases has been also subject to considerable pressure, because the troilite is in a laminated form, and has the characteristic structure found after great pressure.—*Comptes Rendus*, cxl., No. 2.

* A Paper read before the Royal Society, December 15, 1904.

† A plate of the spectrum to which this communication refers will, it is hoped, be published in another place.

* In a still purer specimen from M. Urbain, recently received, these impurities are absent.

THE

THEORY OF THE INCANDESCENT MANTLE.

By VIVIAN B. LEWES,
Professor of Chemistry, Royal Naval College, Greenwich.

EVER since the epoch-making discoveries of Baron von Welsbach, which commenced in 1885 with the method of forming a mantle of refractory oxides that should fit the flame, which were continued by the discovery in 1886 of the transcendent virtues of thoria as a mantle basis, and which culminated in 1891-2 in the still more wonderful discovery of the power exercised by a trace of ceria in awakening the marvellous power of light emissivity which the mantles of to-day possess, speculation has been rife as to the causes which lead to the incandescent mantle giving us 20 candles of light per cubic foot of gas consumed, instead of the small fraction of that amount obtainable when we rely upon the incandescence of carbon particles in the flame for the production of light.

From the time when Murdoch first showed the wonders of his "flame without a wick" to the admiring rustics of Redruth, down to the present day, the source of the light emitted by an ordinary hydro-carbon flame has afforded a happy hunting ground, as well as battlefield, for scientific observers, and although everyone now admits that it is the incandescence of minute carbon particles within the flame that emits the light, diversity of opinion still exists as to several minor points, whilst the incandescence of the mantle offers a still wider field for speculation and research.

It was the discovery of the lime-light in 1826 which first called attention to the great light-giving power of certain unburnable refractory substances, when heated to a high temperature, and Goldsworthy Gurney having shown that a lime cylinder could be raised to incandescence by the flame of the oxy-hydrogen blowpipe, Drummond utilised the light shortly after in a survey of Ireland, and from that day to this it has been a faithful servant to the lanternist when the electric arc was unavailable.

It is clear, however, that the heat required to raise such a mass of material as the lime cylinder to incandescence is very considerable, as radiation and conduction both tend to dissipate the heat, and prevent the necessary temperature being reached.

That this is so can at once be seen by holding a coil of thick platinum wire in a Bunsen flame, when the metal is hardly heated to visible redness; a wire of medium thickness, however, is quickly raised to bright redness, whilst a thin wire is rapidly raised to incandescence, and in a few minutes melts in certain parts of the flame.

Realising this, attempts were made to reduce the size of the mass to be heated, and buttons of zirconia and of magnesia were, for a short time, used for street-lighting in Paris, an oxy-coal gas flame yielding the necessary temperature. The high cost and constant renewals needed, however, soon led to the abandonment of this attempt at incandescent lighting, and the next step forward was the discovery by Talbot in 1835, that even the feeble flame of the spirit-lamp sufficed to heat lime to high incandescence, if only it could be sufficiently finely divided, and this he did by soaking blotting-paper in a salt of calcium and incinerating it.

Up to this time it was only the spirit-lamp and oxy-hydrogen blowpipe which gave flames free from carbon particles, but in 1848, Gillard introduced the intermittent process of making water-gas, and desiring to use it for lighting as well as heating, made a mantle of fine platinum gauze to fit the flame. For a time he obtained excellent results, but the surface of the metal soon became eroded by the flame gases, and the light-giving power fell to a useless point, and although inventors have resuscitated the platinum mantle in various forms since Gillard's early attempts, the same trouble has in every case proved fatal.

Early in the fifties, the idea of making a non-luminous gas flame by mixing coal-gas with a certain proportion of the air needed for its combustion before burning, led

Bunsen to enrich the gas industry with the burner which bears his name. The construction of the atmospheric burner really marks an epoch in the history of the gas industry, second only to the discovery of the mantle to use with it, as it opened up a field for gas for heating purposes, which is now almost as important as for lighting.

Early in the eighties, the idea of the incandescent mantle again came to the front, and the Clamond basket and a revival of the platinum mantle paved the way to the discoveries of Dr. Auer von Welsbach, which were destined to revolutionise our methods of gas-lighting, and even gas manufacture.

Dr. Auer was, in the early eighties, studying the reactions and separations of the rare earths, in which spectroscopic determinations play an important part, and desiring to obtain a greater illuminating effect than was produced by placing some of the material on platinum wire, tried the effect of impregnating cotton with a solution of the metallic salt, and then burning it in a Bunsen flame, when he found that the organic matter burnt away and left a perfect image of the cotton fibres, composed of oxide of the metal taken, and that this oxide skeleton glowed brightly in the flame, this being especially the case with lanthana, which emitted so much light that the idea entered his mind of using a cotton fabric impregnated with a salt of lanthanum for practical lighting. This, however, proved a failure, as the oxide absorbed moisture and carbon dioxide from the air, and rapidly crumbled away. A mantle of magnesia and lanthana was then tried, but, although it gave a good light, it soon became fused and glassy on the surface, and the light given diminished very rapidly. Zirconia in admixture with some of the rare earths was next tried, and better results obtained, as the result of which the 1885 patent was taken out.

Continuing his experiments, Dr. Auer found that the oxide of the metal thorium—thoria—when added to other oxides of the rare earths, brought up their light-giving power, and also added to the strength of the mantle, but although the use of thoria was protected by the 1886 patent, the mantles were so unsatisfactory that no success was achieved with them, and no uniformity of result could be obtained. For several years it looked as if incandescent mantle lighting was to be a dismal failure, but then Dr. Auer made a research upon thoria, and found that the more he purified it, the less light did mantles made with it give, and finally came to the great discovery that it was an admixture of a trace of ceria with the thoria which endowed it with its wonderful power of emitting light. This led to the adoption in 1892 of the mixture of 99 per cent thoria and 1 per cent ceria, a mixture which the thousands of attempts made since have failed to improve upon.

The oxides to be used in the form of mantles must have certain qualifications which are very difficult to find, hence the number usable is very limited. The oxide must be unaffected by atmospheric influences, must be sufficiently refractory not to melt or even seriously soften at the temperature of the flame, and must be non-volatile, whilst during the conversion by the process of burning off of the nitrate-laden cotton into the oxide skeleton, shrinkage must not be excessive.

These requirements are most nearly satisfied by the oxides tabulated below, and a glance at the recorded illuminating powers, as given by mantles made with the commercial salts and with carefully purified salts, shows the wonderful influence in the power of emitting light which traces of foreign oxides impart to the mantles.

When one comes to test the oxides in this table for shrinkage, duration, and strength, one finds that three only of them are fit to be employed as, what one may term, the basis of the mantle. These are zirconia, alumina, and thoria, but on making mantles with them, it is found that zirconia in the hottest part of the flame is liable to considerable and rapid shrinkage, whilst with alumina, not only is there shrinkage and semi-fusion, but also slow volatilisation, so that the life of the mantle is

Light Emitted per Cubic Foot of Gas by Various Oxides.

Oxide.	Pure.	Commercial.
Metals—		
Zirconia	1.5	3.1
Thoria	0.5	6.0
Earth metals—		
Cerite earths .. Ceria	0.4	0.9
Lanthana	—	6.0
Yttrite earths .. Yttria	—	3.2
Erbia	0.6	1.7
Common earths .. Chromium oxide	0.4	0.4
Alumina	0.6	0.6
Alkaline earth metals—		
Baryta	3.3	3.3
Strontia	5.2	5.5
Magnesia	5.0	5.0

gradually shortened by the threads of oxide structure near the base of the mantle slowly wasting away. On the other hand, thoria practically occupies a position by itself as the ideal basis for the mantle, being readily shaped at the temperature of the blowpipe flame, and resisting the action of temperature in the atmospheric burner for a considerably longer period than any other known oxide, whilst in the conversion of a fabric saturated with thorium nitrate into thoria, the shrinkage is smaller than with any other substance.

The factor which gives it its pre-eminence as the basis of the mantle is that in the conversion of thorium nitrate into thorium oxide by heat, an enormous expansion takes place, the thorium oxide occupying more than ten times the volume of the nitrate taken. This, of course, means that the mass is highly spongy, and contains an enormous number of little air cells, which must render it a splendid non-conductor. As has already been stated, a mantle made with thoria alone gives practically no light, but the power of light-emissivity in it is awakened by the addition of a small trace of ceria, and careful experiment shows that as ceria is added to it, little by little the light which the mantle emits grows greater and greater, until the ratio of 99 per cent thoria to 1 per cent of ceria is reached, when the maximum illuminating effect is obtained, and that the further addition of ceria causes this to gradually become less, until when some 10 per cent of ceria has been added the light given by the mantle is again almost inappreciable.

When cerium nitrate is converted by heat into cerium oxide the expansion which takes place is practically nil, the ceria obtained from a gm. of the nitrate occupying about the same space as the original nitrate. The result is that although by weight the ratio of ceria to thoria is as 1 to 99, by volume it is only as 1 to 999, and we have now to see the theories which have been put forward to explain the wonderful power of light-emissivity awakened by these excessively minute traces of the excitant.

Dr. Drossbach, early in the controversy, ascribed the power of the mantle to some special action of the ceria in converting heat rays into light, while Drs. Killing and Moschelles came to the conclusion that as ceria formed two oxides, the particles of ceria in the mantle, by rapid transition from one condition of oxidation to another, caused local spots of temperature, due to more rapid oxidation at those points. Dr. Killing also favoured the theory of catalytic action, afterwards warmly supported by Dr. Bunte, whilst during the last few years Le Chatelier, Nerst and Bose, Thiele, Muthmann, Féry, White, Traver, Russell, and others have done an infinite amount of work upon the subject, whilst Drossbach, Killing, and Bunte have again attacked the subject from altered points of view.

The theory which always appealed most to me was the catalytic theory as enunciated by Dr. Bunte, and now that he has formally discarded it in favour of a theory of selective radiation, I feel more than ever inclined to champion it, as it undoubtedly plays an important part in raising the temperature of the mantle.

I will not spend any time on the dual oxide of cerium theory, as, although it is the one favoured by Baron Welsbach himself, I know of no satisfactory proofs that have been adduced in its favour, as apart from simple catalytic action, but I will devote myself to a consideration of the catalytic theory and the more modern work on temperature and radiation.

The general definition of catalytic action in the layman's mind is that it is a convenient word to cover a class of actions which the chemist is unable otherwise to explain, but the special form of catalysis with which I wish to deal is of a less obscure order. If we take a roll of platinum foil and heat it to redness over the gauze of a Bunsen burner, and then extinguish the flame and allow the current of mixed coal-gas and air to flow over it before it has cooled to too low a temperature, it again commences to glow, and will remain incandescent as long as the flow of gas and air over its surface continues, this phenomenon being produced by the metal condensing hydrogen from the coal-gas and oxygen from the air on its surface, and rendering them so chemically active that they combine on the surface of the metal below the ignition point of the mixture, and emit sufficient heat to render the foil red-hot. A catalytic action of this kind undoubtedly takes places with the Welsbach material. Dr. Bunte showed, some years ago, that ceria had the power of lowering the temperature at which hydrogen and oxygen combined, by about one-half—from 649° C. (1200° F.) to 315.5° C. (600° F.), and one knows an action of this description is always intensified by increase of surface in the substance acting, so that in the platinum experiment, if spongy platinum instead of foil be used, it will ignite the gaseous mixture without previous heating, and the trace of finely divided ceria on the surface of the thoria in the mantle is so active, that, under proper conditions, the mantle can be kept luminous in a stream of coal-gas and air. Dr. Luggin first showed this, and by a slight modification of his experiment it can be shown with beautiful clearness.

A mica chimney is fixed over the mouth of a large Bunsen burner, so as to form a prolongation of the tube, and the mixture of gas and air is lighted at the mouth of the chimney, the air supply being regulated to give a non-luminous flame. An ordinary Welsbach mantle is then hooked by its loop on to a stout platinum wire, and is held in the burning mixture of gas and air at the mouth of the chimney, where it glows and emits light in the usual way, and on now lowering it down through the flame into the mica chimney below, it continues to incandesce in the cold current of gas and air.

It is quite clear from this experiment that the catalytic vigour of the Welsbach mantle is sufficient to keep it incandescent in the mixture of gas and air, without the exterior heating of the flame, and it seems impossible, therefore, to ignore this action when the mantle is rendered incandescent under ordinary conditions. Before attempting to explain why this particular mixture of thoria and ceria, and no other, gives the highest possible illumination, it will be well to examine the other theories that have been brought forward.

If the Welsbach mixture were endowed with a special power of translating heat into light, proof of this ought easily to have been obtained by the way in which rare oxides and mixtures behave when heated out of contact with air. Dr. Bunte found that in trying this experiment there was a very small difference in the noticeable light radiation from bodies of such widely different light-emissivity as carbon, magnesia, thoria, or the mixtures used in the Welsbach mantle.

In order to prove this, Bunte took a thick walled tube or retort carbon, the walls of the middle portion of which were reduced to a thickness of 0.059 inch for a length of about four inches, and on passing a strong current of electricity through the retort carbon cylinder, the resistance of the thin walled portion caused it to be heated up to whiteness, the temperature attained being estimated by him to be over 1999° C. (3360° F.). The tube was prevented from burning

away at this highly-heated point by being coated with magnesia, over which an outer wrapper of asbestos paper was pressed, and in the interior of this tube small square prisms of magnesia were placed, coated with the substances to be examined, each prism being compared side by side in the hottest portion of the tube. The conditions existing could be observed through a small sight-hole at the end of the carbon tube.

By using double prisms, one of which was coated with the substance to be tested, and the other with a standard substance of known composition, it was found that practically little or no difference existed between the various materials tested. This point was also confirmed by some very interesting experiments made by Mr. Swinton, in which he enclosed various mantle materials in a vacuum tube and submitted them to cathode rays, by which a very high temperature can be obtained, capable of raising finely divided carbon to incandescence, and fusing platinum into into glass. Using mantles made up of small squares of ceria and thoria alone, and mixed in varying proportions, he found that, although the mixture of 99 per cent thoria and 1 per cent ceria in a vacuum heated up to incandescence more rapidly than pure thoria alone, and on stopping the discharge cooled down more rapidly, its incandescence was only very slightly greater than that of the thoria alone.

It is clear that either Bunte and Swinton were in error in their observed results, or else that the idea of the Welsbach mantle having any peculiar power of converting heat rays into light must be discarded, as otherwise the same differences would have been noted when the materials were heated out of contact with air, as is shown in the flame.

In 1898, Le Chatelier and Boudouard published a paper in the *Comptes Rendus*, in which they claim that the luminosity of mantles may be explained by the ordinary laws of radiation, and from data obtained by heating a flattened thermo-couple coated with various oxides, and noticing the radiations as compared with those given by melting platinum as unity, they conclude that the substance of the mantle possesses at its working temperature an unequal emissive power for the different kinds of rays; it is, therefore, to be regarded as at that temperature a coloured body. Its useful incandescence results from the fact that its very high emissivity, near to unity, for blue, green, and yellow rays, is less for the red, and doubtless still more feeble for the ultra-red. The proportion of energy radiated as visible rays is consequently very high; nevertheless, the absolute amount of energy radiated as light is smaller than that which would be diffused by a black body raised to the same temperature. But a black body heated under the same conditions, and with the same area of radiating surface, would attain only a very much lower temperature, and would also have only a very low illuminating power.

In 1900, Professors Nernst and Bose also concluded that the high illuminating value of the mantle could be explained solely by selective radiation of the Welsbach mixture, at the temperature of the Bunsen flame, and in order to ascertain whether the flame gases have any specific effect upon the emission of light by a Welsbach mantle, the two experimenters endeavoured to find out whether there was any difference between the radiations from a Welsbach mantle fibre heated in the usual way and those from a similar fibre heated by an electric current. At equal temperatures the radiations were found to be almost identical with thin fibres. Thicker rods brought about differences, which could, however, be simply explained through the heating by the flame being from without, whilst that by the current was from within. The following table gives the data of this comparison:—

Wave lengths.	Flame heating.	Electric heating.	Ratio.
688	0.770	0.790	1.03
589	1.000	0.987	0.99
516	1.36	1.37	0.99
477	2.39	2.34	0.98
447	4.21	4.09	0.97

In conclusion, they give their theory as follows:—Since the substance of the mantle emits but little red light or ultra-red rays, and thus gives off but little energy in the form of heat, the mantle can, therefore, completely absorb the high temperature of the gas flame, and, in consequence, emit a relatively greater amount of light.

In 1902, Messrs. White, Traver, and Russell, of the University of Michigan, published a paper on the "Theory of the Incandescent Mantle," which was supplemented later in the year by another on the same subject by White and Traver. In these papers they describe the experimental determination of the temperatures existing in the mantles, and in the flame heating them, by means of the Le Chatelier thermo-couple, and experimented with a pure thoria mantle as well as with one of the ordinary Welsbach mixture. They found that the pure thoria mantle attained a temperature of 1510° C., and had an illuminating value of 1.2 candles per cubic foot, whilst the Welsbach mantle only reached a temperature of 1401° C., and gave 15.7 candles a foot, which they point out is in direct contradiction to the theories of Nernst, Le Chatelier, and their pupils, who hold the illumination of the mantle to be a function of temperature alone. They then repeated the experiments, using pats of ceria, thoria, and the mantle mixture, in which thermo-couples were embedded, and found that the highest temperature was attained in all experiments from pats of pure thoria, which emitted no light, a result in direct contradiction to Le Chatelier, who found that a couple coated with Welsbach mixture attained a higher temperature than one coated with thoria alone, and it was upon this that he founded his theory. The authors conclude that the exceptional efficiency of the Welsbach mixture is due to a solid solution of ceria in the thoria, and that it has the power of transforming the heat of the flame into light more economically than any other substance yet known.

This paper is of exceptional value on account of the care taken by the authors in proving that fair relative values of mantle temperature can be obtained by judicious use of the thermo-couple, and also for the first recognition of the fact that the thoria mantle is at a higher temperature than the Welsbach mantle. There are, however, two or three weak points in the paper, whilst the conclusion carefully avoids the point at which all the theorists break down, *i.e.*, why 0.5 to 1.5 per cent of ceria and no other proportion should have the wonderful effect it possesses of awakening the light-giving power of the mantle.

In taking the mantle temperatures, they employ a burner intended for use with a chimney, and as the latter interferes with the manipulation of the thermo-couple, they discard the chimney. This does away with the draught round the mantle, and instead of the flame burning as it should on the surface of the mantle, it has its outer zone of combustion thrown outside the mantle, and that this is so is shown by the Welsbach mantle only giving 15.7 candles per cubic foot of gas instead of 19, as it would have done probably with a chimney on. Under these faulty conditions they take the temperatures of the mantle and the hottest part of the flame outside it, and find the flame considerably hotter than the mantle. Realising that the conditions are not normal, they then use forced draught, and get results of the same character, but here again the conditions are not those existing with the burner used as intended, and the soft combustion on the surface of the mantle essential for the best results would not be obtained.

Dr. Killing, in 1903, attempted to solve the problem of the mantle by measuring the relative heat radiations of pure thoria mantles and Welsbach mantles in the Junker calorimeter, and found that the addition of 1 per cent of ceria to a mantle increased the heat radiated by 1.4 per cent, and confirmed this figure by direct thermometric measurements, and he concludes from this that ceria in the Welsbach mixture displays a specific power of increasing the radiation of the mantle.

In 1903, Dr. Bunte read a paper before the Chemical Meeting in Berlin, in which he formally renounced the

catalytic theory, and adopted the theories of Nernst and Le Chatelier on the strength of experiments made under his direction by Dr. Eitner and Herr Schmidt. Eitner first determined the temperature of various points on the surface of a naked Bunsen flame, and then, having put a Welsbach mantle on it, took the temperatures at the same heights above the burner head as those at which the temperatures of the flame had been determined, and found that the flame was considerably hotter than the mantle.

Experiments in which the temperatures of the atmospheric burner flame burning without a mantle are compared with the temperature of the mantle at the same heights above the burner mouth, are absolutely fallacious and useless for two reasons. In the first place, a simple observation of the shape of the flame and of the mantle shows at once how different they are, and that, with the exception of the first few millimetres at the base, the flame and mantle could not be in contact unless the presence of the mantle altered the shape of the flame to a considerable degree, which would also alter its temperature; and, in the second place, in all ordinary atmospheric burners the uprush of the gas in the suction tube draws in the air necessary for the primary actions which give the inner zone to the Bunsen flame, and when the burner is working without a mantle this is arranged to give a hot flame, *i.e.*, as large a proportion of air to gas as the structure of the burner will allow. The moment, however, that the mantle is put on, the heated structure throws a back pressure on the current of gas and air, which in no way affects the gas, which is driven forward by the pressure in the mains at the same rate as before, but entirely acts in reducing the air supply, which at once falls by 12 to 30 per cent in quantity, according to the burner used.

This has given rise to many fallacious ideas as to what burners are really doing as regards aeration, some high power burners being claimed to give the full ratio of 6 of air to 1 of gas, whilst, in fact, the ratio is not much more than half that amount. Some years ago I showed that the best mixture of air and gas, *i.e.*, that which gave the maximum illumination from a mantle, was for gas of the quality of London gas 5.25 to 1, and within the last year this has been confirmed by Herr Winkler, who gives 5.3 to 1; but such proportions are only attained where both air and gas are either under pressure or suction, and if the ratio of air is increased above this point the light from the mantle falls, unless the burner be converted into what is practically a blast blowpipe. For example, a Lucas lamp is claimed to give over 6 of air to 1 of gas, and does so if tested without a mantle, but directly it is tested with a mantle burning under normal conditions, it is found that the ratio is under 5 to 1.

It is clear, therefore, that such tests as those made by Dr. Eitner are worthless as showing the relation between the temperature of the mantle and the flame, or proving that the mantle is cooler than the flame which heats it.

Herr Schmidt made spectro-photometric investigations on thoria-ceria mixtures at various temperatures, and found that the higher the temperature the bluer becomes the light yielded by thoria, whilst the same thing is observed with mixtures of the two oxides all the time the ceria is below 0.5 per cent. From 0.5 to 1.5 per cent of ceria the red rays and illuminating power increase, but beyond that percentage the colour approaches nearer to pure ceria, and the illuminating power decreases. These two sets of experiments lead Dr. Bunte to adopt the theory that the lighting effect of the mantle is mainly a consequence of its selective radiation, and to discard his previous belief in catalytic action, owing to Eitner's experiments showing the mantle to be cooler than the flame.

Certainly, one of the most valuable and complete researches on the mantle is that by M. Chas. Fery published at the close of 1902, and the conclusion he arrived at is that a mantle of cerium gives no light because it has so great a power of heat radiation that it is impossible to raise its temperature sufficiently in a flame (the temperature of which is limited by the phenomena of dissociation) to

endow it with the power of giving light. When, however, the ceria is sufficiently attenuated by sub-division in a thoria mantle, it can be raised to the required temperature, and the light of the Auer mixture is the result.

In 1903, M. E. Sainte-Claire Deville published some experimental results on mantles which led him to support the theory enunciated by Fery, and a number of experiments have been made in the laboratories at Greenwich during the past few months, the general results of which I will state here, but full details of which I hope to publish shortly.

When mantles of thoria, ceria, and various mixtures of the two are made of exactly the same size and shape, which can be done by using a Buhlmann burning-off apparatus, and when these mantles are tested in a properly regulated Kern burner so as to avoid the use of a chimney, all conditions being kept exactly the same for each, it is found that the flame only extends a millimetre or two beyond the mantle, and that the thoria and 99 per cent thoria with 1 per cent ceria are the only mantles that are heated to a temperature slightly higher than is found in the flame 1 m.m. from the surface of the mantle. The temperatures of the mantle and flame, however, vary enormously with the character of the mantle, and the following table gives the mantle temperature and flame temperature taken 6 m.m. above the rim of the burner, a point at which the mantle is just free from disturbing elements, and where the maximum light is being emitted. There is also given a relative radiation value for the mantles obtained by a thermopile at a fixed distance from them, all measurements being taken with every possible precaution to ensure accuracy.

The thoria was not absolutely pure, containing 0.1 per cent ceria, so that the mantle gave 3.4 candles per cubic foot of gas consumed instead of 0.5, and this probably makes the radiation value higher and the mantle temperature lower than it would be for pure thoria.

	Thoria, 99.9 per cent. Ceria, 0.1 per cent.	Thoria, 99 per cent. Ceria, 1 per cent.	Thoria, 99 per cent. Ceria, 10 per cent.	Ceria.
Temperature of mantle				
6 m.m. above burner rim	1610	1570	1335	1125
Temperature of flame				
1 m.m. from mantle in same spot	1590	1560	1350	1130
Average temperature of mantle up to height of 52 m.m. from burner	1468	1441	1209	1020
Average temperature of flame over same zone	1430	1439	1234	1032
Illuminating power, candles per cubic foot of gas	3.4	20.0	3.3	nil
Radiation value	140	152	218	231

The conclusions which appear to me clear from these figures and the various experiments I have described are that the thoria, owing to its non-conductivity due to its porous condition, its low specific heat, and low radiation power for heat, can be raised to the temperature of the flame, whilst catalytic action on the still unburnt flame gases and air raises it a few degrees even above this point. Ceria when added in quantities up to 1.5 per cent by weight, or 0.15 per cent by volume, does not interfere with these conditions, but by its still higher catalytic powers tends to focus the combustion of the extremely attenuated combustible constituents of the flame gases on the widely distributed ceria particles, and by this localisation raise them to a far higher temperature than the mantle, a temperature, however, which cannot be detected by the thermo-couple, which only gives the average temperature of the mass with which it is in contact, and fails to show the temperature of the 0.15 per cent of ceria. Addition of more ceria to the mixture causes such a rapid cooling of both mantle and flame by radiation that the light at once

begins to fall, and by the time 10 per cent of ceria is in the mixture, the mantle gives us no more light than a thorium mantle, but a much increased heat radiation.

As to the portion of the spectrum to which the light waves emitted by the ceria at the temperature attained by the finely divided particles in the mantle belong I have no personal knowledge, and am quite prepared to accept the evidence adduced by Le Chatelier, Nernst, Schmidt, and others, in which case catalysis, temperature, and selective radiation all play their part in bringing about that wonderful light emissivity which has made the incandescent mantle the saviour of the gas industry.

VOLUMETRIC DETERMINATION OF ACIDS IN SALTS.

By JOHN B. COPPOCK, B.Sc. (Lond.), F.I.C., F.C.S.,
Associate, Nottingham University College.

Preliminary.

THE following determinations were made to show the possibility of quantitatively finding the weight of acid combined with base in some common salts. The use of sulphuretted hydrogen and those salts whose metals give insoluble sulphides, gives the requirements for the carrying out of such determinations.

Salts of the following metals were precipitated by sulphuretted hydrogen:—Lead, copper, bismuth, cadmium, and mercury; the acid being hydrochloric, sulphuric, or nitric.

These determinations, used as exercises in laboratory work, will bring to the mind of the student the reality of the formula for a salt. Volumetric work, being usually undertaken before gravimetric, often lacks in presenting the facts of the quantitative relation of acid and base; these exercises supply the deficiency.

Method.

One uniform method has generally been adopted in the determinations. The salt is weighed out, dissolved in water in most cases, and the base precipitated as sulphide by well washed sulphuretted hydrogen; washings and filtrate being collected together for titration; this being done with methyl-orange as indicator and N.NaHO as alkali.

Determination of Nitric Acid in $\text{Pb}(\text{NO}_3)_2$.

8.275 grms. of pure lead nitrate, prepared by dissolving lead oxide in nitric acid, was dissolved in 250 c.c. of water, broken up into fractional quantities as shown below, and completely precipitated by sulphuretted hydrogen. The lead sulphide was filtered off and washed thoroughly.

Results.

Solution precipitated.	N.NaHO for neutralisation.	Nitric acid found.	Nitric acid calculated from formula.
C.c.	C.c.	Grm.	Grm.
25	5	0.315	0.3132
25	5	0.315	0.3132
50	10	0.630	0.6264

Determination of Hydrochloric Acid in HgCl_2 .

Five grms. of pure mercuric chloride were dissolved in 250 c.c. of water. Fractional quantities were precipitated with sulphuretted hydrogen, filtered, and washed. The gas was passed until the precipitate was thoroughly black. The sulphide (HgS) subsides well.

Solution precipitated.	N.NaHO for neutralisation.	Hydrochloric acid found.	Acid calculated from formula.
C.c.	C.c.	Grm.	Grm.
50	7.35	0.268	0.262
50	7.35	0.268	0.262
50	7.35	0.268	0.262

Determination of Sulphuric Acid in $\text{CdSO}_4 \cdot 4\text{H}_2\text{O}$.

Three grms. of the salt were weighed out and dissolved in 250 c.c. of water. Fractional quantities were then precipitated by sulphuretted hydrogen.

Results.

Solution precipitated.	N.NaHO for neutralisation.	Sulphuric acid found.	Acid calculated from formula.
C.c.	C.c.	Grm.	Grm.
50	4.25	0.21	0.208
50	4.25	0.21	0.208
100	8.5	0.42	0.416

Determination of Nitric Acid in $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$.

Owing to the decomposition of bismuth salts by water, it is impossible to start with a water solution. The passage of sulphuretted hydrogen converts the oxy-salt into sulphide; hence the acid can be titrated. An alternative method is to add a known volume of N.HNO_3 and to subtract the amount added in the final titration.

0.5 gm. of the salt was weighed out and treated with sulphuretted hydrogen, filtered, and washed.

Results with First Method.

Quantity of salt precipitated.	N.NaHO for neutralisation.	Nitric acid found.	Acid calculated from formula.
Grm.		Grm.	Grm.
0.5	3.15	0.198	0.195
0.5	3.15	0.198	0.195
0.5	3.15	0.198	0.195

Results with Nitric Acid Method.

0.5 gm. of $\text{Bi}(\text{NO}_3)_3$ was weighed out and dissolved in water and nitric acid; 10 c.c. of acid being necessary, which, by a previous titration, was found to be equal to 36.5 c.c. N.NaHO.

Quantity of salt dissolved.	N.NaHO for neutralisation.	N.NaHO for salt acid.	Nitric acid found.	Acid calculated from formula.
Grm.	C.c.	C.c.	Grm.	Grm.
0.5	39.6	3.1	0.1953	0.195
0.5	39.5	3.0	0.189	0.195

Determination of Sulphuric Acid in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

This proved to be the most difficult salt to carry on the determinations, which is rather unfortunate, on account of its having such a well defined amount of water of crystallisation, other salts of this group varying more easily in water of crystallisation.

Small quantities must be operated upon for quick filtration, owing to the following difficulties:—The solubility of copper sulphide in sulphuretted hydrogen solution, and the ready oxidation to sulphate. The sulphate passes through the filter, and, falling into a solution containing sulphuretted hydrogen, gives more acid liberated, and makes results too high. The titration is rendered rather difficult.

However, on using small quantities of salt and working exactly as in previous methods, the following results were got. 2.35 grms. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were dissolved in 100 c.c. of water, and 25 c.c. of solution taken for each determination:—

Solution precipitated.	N.NaHO required for neutralisation.	Sulphuric acid found.	Acid calculated from formula.
C.c.	C.c.		
25	4.71	0.230	0.231
25	4.8	0.235	0.231
25	4.8	0.235	0.231

Chemical Laboratory,
Kendal Technical Schools.

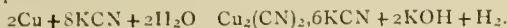
Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 6th inst., The Duke of Northumberland, K.G., F.R.S., President, in the Chair. Lieut.-Col. H. E. Gaultier, Mr. E. P. Harvey, Mrs. Ludwig Mond, Dr. Tcherniac, and Dr. Evelyn C. B. Wilbraham, were elected Members.

ACTION OF A SOLUTION OF CYANIDE OF POTASSIUM ON DIFFERENT METALS.

By ANDRÉ BROCHET and JOSEPH PETIT.

CYANIDE of potassium has the curious property of dissolving most metals. According to the nature of the metal, this action may take place either with the fused salt in the presence of steam, or with the solution at the ordinary temperature or at boiling point. Following up our researches on the solution of metals in cyanide of potassium under the influence of an alternating electric current (*Bull. Soc. Chim.*, Series 3, vol. xxxi., p. 359), we examined the spontaneous action of cyanide of potassium as much as possible under identical conditions. Our experiments were carried out on a solution of 4 grm.-molecules per litre. For details we must refer the reader to a more complete paper in the *Annales de Chimie et de Physique*, and in the present note we give simply a summary of the most interesting results.

Aluminium and magnesium are attacked in a most energetic manner, even in the cold. The attack of other metals is much less lively, and only copper and zinc give off hydrogen to any appreciable degree. In the former case the salt is transformed integrally according to the equation:—



With zinc the attack is arrested on account of a very slightly soluble deposit of the double cyanide of zinc and potassium on the strip of metal, $[\text{Zn}(\text{CN})_2, 2\text{KCN}]$.

In both cases the solution takes place much more quickly at boiling temperature.

With other metals the attack in the cold is insignificant, and sometimes it is necessary to wait for several days before noticing an appreciable loss of weight. At the boiling temperature the attack is more marked, and corresponds to 1 or 2 milligrams. per hour.

With certain metals—cadmium, silver—the attack goes on with the aid of the atmospheric oxygen, and is concentrated almost entirely on that portion of the strip of metal immediately below the surface of the liquid.

Mercury is not attacked, and amalgamation impedes the solution of the metals; thus, other conditions being the same, amalgamated copper dissolves about ten times more slowly than the pure metal.

Platinum is the metal upon which the action of cyanide of potassium is the most interesting.

In the year 1876, Sainte-Claire Deville and Debray (*Comptes Rendus*, 1876, lxxvii., p. 241) showed that platinum was dissolved in fused cyanide of potassium in the presence of steam; they announced that the solution attacked the metal equally well in the form of strips or sponge, and at the boiling temperature, but they did not give any figures. Glaser (*Zeit. f. Elektroch.*, 1903, vol. ix., p. 11) made some experiments on the solution of the sponge. We thought it advisable to try to what degree the solution of the metal in strips took place. With this object we took a strip having a total surface of 110 sq. centims., and after having washed it well in nitric acid and cyanide of potassium, we rinsed, dried, and weighed the metal; it was then placed in a wide-mouthed flask with 150 c.c. of a solution of cyanide of potassium kept at the boiling point. The flask was fitted with a vertical condenser. The strip of platinum was withdrawn from time to time, and lost weight as follows:—

After 2 hours	..	..	..	0.033 grm.
" 10 "	..	..	..	0.187 "
" 18 "	..	..	..	0.248 "

This strip of metal had then become dull over a large part of its surface. The diminution of the attack was due to the weakening of the solution, which after ten hours contained only 25 per cent of the original amount of cyanide, and after eighteen hours only 9 per cent, owing to its transformation into formate of potassium and am-

monia. The strip of metal heated again with fresh cyanide then lost:—

After 4 hours	..	..	..	0.1175 grm.
" 8 "	..	..	..	0.2194 "

We see from these figures that polished platinum is more difficult to attack than rough platinum, and that in the latter case the attack reaches 0.030 grm. per sq. decim. per hour.

In the cold, solution does not take place at all. A strip of platinum having a surface of 2 sq. decims. did not vary by 0.001 grm. during six months while it was under examination.—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 23.

ON SOME CUPRAMMONIUM SULPHATES.*

By DAVID W. HORN and EDYTHA E. TAYLOR.

(Continued from p. 52).

II. Preparation of the Salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$.

A. Berzelius' Method.—The preparation of this salt is said to have been described first by Stisser (1693; see Roscoe and Schorlemmer, II., i., 339). Berzelius, however, was the first to assign a formula to it. The method of preparation advised by him consists in treating a solution of copper sulphate with an excess of ammonia water and adding alcohol to the resulting purple solution. If the alcohol be carefully poured upon the purple solution, crystals of the salt form at the surface of contact of the two liquids. If the alcohol be slowly added and mixed with the purple solution, the salt separates as a pulverulent crystalline deposit.

We have found that in any case the salt is very unstable after it is removed from its mother-liquor. Only small quantities of it can be dried between filter-papers or on unglazed porcelain plates without considerable decomposition. This decomposition is clearly indicated by the odour of ammonia above the salt. The following are analyses of small quantities of the salt dried thus as quickly as possible:—

	Weight of salt taken for analysis.	Weight of ammonia found.	Percentage of ammonia found.	Percentage of ammonia calculated for $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$
	Grm.	Grm.		
I.	1.1978	0.3296	27.51 (T)†	27.75
II.	0.6519	0.1797	27.57 (T)	

If larger quantities are dried, even though they are first washed with absolute alcohol, the decomposition has time to go much further, as is seen from the following analyses of a specimen of perhaps 30 grms.:—

	Weight of salt taken for analysis.	Weight of ammonia found.	Percentage of ammonia found.	Percentage of ammonia calculated for $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$
	Grm.	Grm.		
	0.4979	0.1298	26.07 (T)	27.75
	0.5022	0.1326	26.50 (T)	
	0.4852	0.1245	25.66 (T)	

If the salt is prepared in large crystals, as it readily can be, and the surfaces of these are quickly dried with filter-paper, a pure product is not obtained, because the mother-liquor is occluded in large amounts by the crystals.

Bouzat prepared crystals of this salt for use in his calorimetric studies, by cooling a hot concentrated solution of it and quickly drying the crystals that separated between filter-paper. His methods of analysis are not described in his paper, but the analyses for ammonia of his preparation gave results surprisingly like those we obtained by analysing the same salt dried in the same way, but known by us to have partly decomposed in the drying. He found for ammonia 26.25 and 26.45 per cent (*Ann. Chim. Phys.*, 1903, [7], xxix., 356). He ascribes to the salt the formula

* From the *American Chemical Journal*, xxii., No. 3.

† All experiments and analyses made by E. E. Taylor will be marked (T).

$\text{CuSO}_4 + 4\text{NH}_3 + 3/2\text{H}_2\text{O}$, which represents a salt containing 26.77 per cent ammonia.

The analysis given by Berzelius is as follows :—

	Calculated for $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$.	Found.
CuO	32.37	32.22
SO ₃	32.55	32.58
NH ₃	27.75	27.89
H ₂ O	7.33	7.31
	100.00	100.00

Though the pure salt cannot be prepared by drying between filter-papers, apparently it can be prepared in some other way.

We prepared a quantity of the salt by Berzelius' method, and quickly transferred specimens of it from its mother-liquor to unglazed porcelain plates in desiccators. The desiccators contained respectively calcium chloride, sulphuric acid, solid potassium hydroxide, and a small vessel of strongest ammonia water and lime. In the first and second desiccators the salt soon became opaque in spots on its surface. In the third, the crystals seemed to change only in colour, though it was found later that they were losing weight slowly at the same time. In the fourth desiccator (over lime), no change in the salt could be seen.

The steady loss in weight of the crystals over potassium hydroxide and ammonia water was observed for two weeks. Several of the crystals were then analysed for ammonia, with the following results :—

Weight of salt taken for analysis.	Weight of ammonia found.	Percentage of ammonia found.	Percentage of ammonia calculated for $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$.
Grm.	Grm.		
0.4989	0.1395	27.97 (T)	27.75
0.4895	0.1372	28.03 (T)	

Under these conditions the salt had apparently taken up more ammonia. We have studied this change in the salt further, and will refer to it later. Kohlschütter has since used this same method for drying the cuprammonium salts used in his investigations (*Ber.*, 1904, xxxvii., 1153—70). Reference to his paper will show that his analytical results for ammonia are also high.

The crystals dried over lime soon ceased to change in weight. Some of the salt thus dried was finely ground and put in a vacuum over lime; it was weighed at intervals with the following results :—

	Grm.
Original weight	0.6736
Weight after thirteen hours	0.6733
Weight after forty hours	0.6733

We then prepared more of the salt by Berzelius' method, precipitating it as a crystalline powder. This was dried over lime and analysed for copper and ammonia, with the following results :—

	Weight of salt taken for analysis.	Weight of copper found.	Percentage of copper found.	Percentage of copper calculated for $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$.
	Grm.	Grm.		
I. Cu	0.6918	0.1785	25.80 (T)	25.86
	0.4882	0.1573	25.73 (T)	
	0.4888	0.1581	25.84 (T)	
	Weight of salt taken for analysis.	Weight of ammonia found.	Percentage of ammonia found.	Percentage of ammonia calculated for $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$.
	Grm.	Grm.		
II. NH ₃	0.3098	0.0860	27.76 (T)	27.75
	0.4184	0.1161	27.75 (T)	
	0.4184	0.1157	27.65 (T)	

These analyses of the purple cuprammonium sulphate are in accord with that by Berzelius, upon which the formula $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ is based.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, January 27th, 1905.

Dr. R. T. GLAZEBROOK, F.R.S., President, in the Chair.

A PAPER on the "Action of a Magnetic Field on the Discharge Through a Gas" was read by Dr. R. S. WILLOWS.

It has been shown previously that a transverse magnetic field, if applied at the kathode, may, in some cases, reduce the potential difference at the terminals of the tube. It is shown in the paper that the pressure at which this decrease commences corresponds to the pressure at which the voltage required to maintain this discharge, under normal conditions, is a minimum. This is also found to be the pressure at which the positive column is first completely striated. Reasons why such action takes place are given.

A paper on the "Action of Radium on the Electric Spark," by Dr. R. S. WILLOWS and Mr. J. PECK, was read by Dr. Willows.

In certain cases the authors have found that the spark from a Wimhurst machine is extinguished by the action of the radiations from radium, and that the current passing is decreased. The action is altogether different according to the direction of the discharge. Using a spark-gap longer than 2 c.m., and making the larger knob, of the machine used, positive, the radiations had practically no influence. With the smaller knob positive the radium, in most cases, extinguished the spark. The phenomenon is found to be due to the action of the β -rays. Röntgen rays do not produce this effect, even if their ionising power at the spark-gap is some thousand of times greater than that of the radium. Lenard rays are, however, effective.

Prof. F. T. TROUTON expressed his interest in the paper, and referred to the fact that the action of the radium depended upon the direction in which the current was passing. He could see no obvious explanation of this.

A paper on "The Slow Stretch in Indiarubber, Glass, and Metal Wires Subjected to a Constant Pull" was read by Mr. P. PHILLIPS.

When indiarubber is subjected to a sustained pull of constant amount it yields at quite a large rate, the stretch at any time (t), after the establishment of the pull, being given by $x = a + b \log t$, a and b being constants for the particular pull exerted. For different pulls b is proportional to the pull. When the pull is removed the indiarubber slowly returns to its original length, the extension still remaining at a time t_0 after the removal being given by $x = b \log \left(\frac{t}{t_0} \right)$, t being the time which has elapsed since

the pull was established. When one pull is added at a definite interval after another, the effect of the two pulls is not exactly the sum of the effects which would have been produced by each separately, but it approaches very nearly to this after a time. When indiarubber is stretched to a fixed length and retained there, the pull required to maintain that stretch diminishes with time, and is given at any time (t) after the initial stretch was established by the law $P = a - b \log t$, b being proportional to the magnitude of the initial stretch. The temperature coefficients of expansion and contraction of indiarubber in tension are quite different. The decrement of the amplitude of vibrations in indiarubber obeys the ordinary law. The first two results, for the slow stretching and slow recovery of indiarubber, have also been established for glass fibres subjected to sustained pull, but the magnitude of the slow yielding is very much smaller.

When annealed wires of copper, silver, gold, or platinum are subjected to a sustained pull, they behave in some ways similarly to indiarubber and glass, but there are some very decided differences. If the pull is greater than a certain amount (in the actual experiments about one-third to one-quarter of the breaking weight) the stretch at any time (t)

after the establishment of the pull is given by the same law $x = a + b \log t$, but below this value of the pull b is zero. This law obtains up to the breaking strain of the wire, b increasing very rapidly a little before the breaking-strain is reached. When the pull is removed there is no appreciable slow recovery like that occurring in indiarubber and glass. Iron and steel wires show themselves to be exceptions to these rules.

Dr. CHREE remarked that a great many experiments had been made upon the subject, and that both exponential and logarithmic formulæ had been proposed to fit the results. It was possible to get very different formulæ which would agree with the results of experiment with equal accuracy. He thought it was important to distinguish between viscous yielding and elastic creep followed by recovery.

Mr. R. APLEYARD expressed his interest in the paper, and especially in the part dealing with experiments on indiarubber. The author had used vulcanised rubber, and the properties of this would not remain constant over any length of time. He had previously suggested that in experiments such as those described, the value of Young's modulus might be variable. This idea was borne out by the results obtained by Mr. Phillips. One of the chief difficulties was the accurate determination of the diameter of the cord or wire under investigation.

Prof. F. T. TROUTON said the experiments described threw a good deal of light upon the subject, and he was pleased that they confirmed the law which Mr. Rankine had obtained for lead. The logarithmic law also applied if the strain was kept constant and the stress varied. This method had the advantage that changes of diameter were obviated. He thought the law was most important, and that there was something fundamental in it.

Mr. A. CAMPBELL referred to the analogy between the experiments described and those on the residual charge of a condenser. The more heterogeneous the mixture which formed the dielectric the more pronounced were the phenomena of the residual charge. Possibly something of a similar nature might hold in the cases of stretching, and he asked the author if he had performed any experiments on alloys.

Mr. PHILLIPS, in reply, said the alteration in the cross section of the rubber during the experiments was very small. There were many things which might affect the accuracy of the numbers which he had obtained, and he did not wish to lay too much stress upon the absolute values given in the paper.

A paper entitled "Determination of Young's Modulus (Adiabatic) for Glass," by CHICHESTER A. BELL, M.B., with an Appendix by C. CHREE, F.R.S., was read by Dr. Chree.

In this paper it is shown that errors in the acoustical determination of Young's modulus for glass, due to irregularities in the rods or tubes employed, may be eliminated by applying to the measured length of each free-free rod a correction given by the formula—

$$\Delta l = \int_0^l \frac{\delta S}{S_0} \cos \frac{2\pi z}{l} dz,$$

in which δS is the difference between the cross section at the point z and its mean value, S_0 , for the whole rod. Theoretical justification for the formula, which is similar in form, but opposite in sign, to that calculated by Lord Rayleigh for slightly irregular fluid columns, is given in the appendix. In practice the correction is found by dividing each rod, after determination of its rate of longitudinal vibration by comparison with a standard steel rod, into ten equal parts, from the weights and lengths of which the values of the cross section, supposed uniform throughout each segment, are deduced. The sum of the differences between these and S_0 for the whole rod, each multiplied by the integral $\int \cos \frac{2\pi z}{l} dz$ between the corresponding length-limits and by $l/2\pi S_0$, gives the required correction. Observations on altogether thirty rods of seven different

samples of glass are recorded. When the rods are not too irregular the corrected products $n \times 2(l + \Delta l)$ for each kind agree so closely that the final mean value of Young's modulus, $4\pi n^2(l + \Delta l)^2$, is probably correct to three figures.

A paper by Dr. BORIS WEINBERG on "Some Methods for Studying the Viscosity of Solids" was taken as read.

The author has been carrying out investigations similar to those described by Prof. Trouton and Mr. Andrews in their paper "On the Viscosity of Pitch-like Substances" (*Proc. Phys. Soc.*, 1903). The details of his experiments are, however, different. He has worked principally with lead, and has employed three distinct methods for determining the coefficient of viscosity. In the first the base of a parallelepipedon of the substance is fixed, and the opposite face is subjected to a stress parallel to its plane. The variation of the angle of shear with time is then observed. In the second method a rod or tube of the substance is subjected to a twist, and the variations with time of the relative angular displacements of different sections are observed. In the third method the substance to be investigated partly fills the space between two coaxial glass tubes, the lower part of the annulus containing mercury. The outer tube is fixed, and a couple is applied to the inner tube, which is capable of turning about its axis. The relative angular displacements of the tubes are then measured. In all cases the observations have been made by the scale of mirror method, and the substances have been examined under the following conditions:—(a) Constant stress, (b) no stress after a finite temporary strain, (c) constant strain, (d) constant rate of variation of the strain. The numerical results and the laws which govern the phenomena, together with their theory, are reserved for a future communication.

THE FARADAY SOCIETY.

THE Eleventh Ordinary Meeting of the Faraday Society was held on Monday, January 30, 1905, at the Institution of Electrical Engineers, Prof. A. K. HUNTINGTON being in the chair.

Mr. JOHN G. A. RHODIN read a paper entitled "Mass Analysis of Muntz's Metal by Electrolysis, and some Notes on the Electrolytic Properties of this Alloy." The reading of the paper was accompanied by experiments.

The first portion of the paper describes an apparatus which was specially designed by the author for the purpose of the accurate and rapid determination of the copper content (which should lie between 60.5 and 61.5 per cent) of Muntz's metal. As about 40 to 60 "heats" of metal are cast every day, and it being necessary to obtain the results within twelve hours of the time of casting, the apparatus had to be such as to enable 100 analyses to be made in twenty-four hours—with a mean probable error of not more than ± 0.1 per cent. The author decided that an electrolytic method would best fit in with these stringent requirements.

The electrodes employed consist of concentric cylinders of very fine platinum gauze, supported by stout frameworks in order to ensure even current distribution. The anode rests on a ring at the bottom of the containing vessel, so that the cathode can easily be slipped away and removed, and both electrodes are held in modified Classen stands. The present installation consists of thirty such unit cells, and current is supplied to them from six pairs of accumulators, each of which supplies current to five pairs of electrodes, through suitable nickelin resistances.

One gm. of the alloy, dissolved in nitric acid, is used for an analysis, and a current either of 0.5 ampère or else of 2.0 ampères is employed for the deposition. In the former case deposition is complete in twelve to fifteen hours, in the latter in three hours. Electrolysis proceeds in three phases:—1. Copper deposition and ammoniacal reduction of nitric acid. 2. Ammoniacal reduction only. 3. Deposi-

tion of zinc. A perfect separation takes place if phase 2 occupies a long time and is unaccompanied by metal deposition. If certain impurities, such as arsenic or nickel, be present they must be removed chemically. The paper describes in detail the actual procedure at the works laboratory, and also includes a table showing the kind of accuracy obtained in cases where re-analyses have been made. Since these analyses in bulk have been made it has been found that they act as an infallible guide to the casters, so that re-melting has now become very rarely necessary.

In conclusion, the author discusses the electrochemical properties of Muntz's metal. The metal is largely used as a sheathing to protect ships' bottom from certain mollusca and algae, and to be successful it should dissolve in seawater just to a sufficient extent as to render the surface poisonous, the best conditions being the equal dissolution of the copper and zinc. The author shows how these may be calculated approximately, by supposing that the electrolytic dissolution rate is proportional to the heat of formation of the ultimate compounds (zinc and cuprous chlorides), and to the conductivities of the metals which dissolve. Assuming that both the chlorides of copper are formed, and taking the mean of the results in the two cases, the best values are found to be 60.811 per cent of copper and 39.189 per cent of zinc, numbers which agree very closely with the results of practical experience. The author is now engaged in exhaustively investigating the *absolute* dissolution-velocity of pure Muntz's metal at a definite temperature, and he adds here a preliminary description of these experiments, describing in an appendix his most recent experiments on the subject. He finds that a binary alloy like Muntz's metal dissolves slowly at first, the velocity then quickly arrives at a maximum, then it falls suddenly—remaining almost constant for some time—and finally a more or less rapid fall again occurs. During the period of constant velocity the surface must alter as the resistance capacity, if the action is galvanic. The seat of E.M.F. must be in the electrolyte, as the constancy of action indicates a steady E.M.F. of considerable magnitude. It is probable that the result is influenced by the actual mass of metal present, relative to that of the solvent. The external pressure certainly exercises a very considerable effect on the reaction-velocity, by influencing the speed with which hydrogen can leave the surface of the metal.

The author promises further communications on the subject.

Prof. HUNTINGTON asked whether the author had considered the question of the best composition of Muntz's metal from the point of view of the constituents of the alloy, and of the critical points of the various combinations formed. He drew attention to the work of Mr. E. S. Shepherd on this subject, and showed the curves he had obtained in his study of the copper-zinc series. What determined whether the alloy would roll hot or not, appeared to be the presence of the compound Cu_2Zn .

Mr. W. R. COOPER thought there was some difficulty in the view that the dissolving action referred to by Mr. Rhodin was galvanic. If that were the case, he did not see how both metals could be affected.

Mr. A. STEVENSON referred to the question of the deposition of bright copper in the presence of colloids.

Mr. RHODIN, in reply, dealt in detail with the point raised by Mr. Stevenson, which he himself had first investigated in conjunction with Sir Joseph Swan. Replying to Prof. Huntington, he said that it was certain impurities which determined whether a Muntz alloy would roll hot. An alloy containing 70 per cent copper could be rolled, if these impurities were not present.

Mr. R. BECKETT DENISON presented a paper entitled "*The Equilibrium between Sodium Sulphate and Magnesium Sulphate.*"

Experiments conducted from the standpoint of the phase rule are described, the object of which was to determine whether the double salt of sodium and magnesium sul-

phates, $2\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4$, which has been described as a naturally occurring mineral, is capable of existence in contact with solution; that is, whether it has been formed in nature by the evaporation of saline waters. The corresponding potassium compound is known to occur in Stassfurt as langbeinit, and it was thought that a detailed investigation might result in the isolation of the sodium langbeinit from solution.

A transition temperature of 59°C . was obtained for the system $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + \text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$, but it was found that only the double salt loewit, $\text{Na}_4\text{Mg}_2(\text{SO}_4)_{15}\text{H}_2\text{O}$, was formed, the usual transition-point (71°) being depressed to 59°C . by saturation with MgSO_4 .

Dilatometer and tensimeter experiments pointed pretty conclusively to the assumption that the compound sodium-langbeinit cannot exist in contact with solution, at least below 100°C ., and hence this substance, if found as a mineral, must be a product of a higher temperature.

Mr. E. KILBURN SCOTT gave a short abstract of his paper on "*Refractory Materials for Furnace Linings,*" which dealt principally with carborundum siloxicon, and electrically-shunk magnesite.

As the paper had not yet appeared in type, the discussion was postponed.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxi., No. 2, January 9, 1905.

Action of very Low Temperatures on the Phosphorescence of certain Sulphides.—F. P. le Roux.—The author's experiments on the action of low temperatures on phosphorescence show that the maximum luminous potential energy which can be induced in any phosphorescent body is independent of the temperature. The circumstance of temperature has an influence only on the velocity of transformation of potential luminous energy into actual luminous energy.

Supposed Demonstration of the Existence of N-rays by Photography with an Insulated Calcium Sulphide Screen.—MM. Chanz and Perrigot.—Two equal masses of lead and tempered steel identically placed with one face against a calcium sulphide screen, and of comparable thickness and insulation, give no different rings whatever the length of the exposure. If, in practical experiments with identical screens, unequal rings are shown, the difference is explained, not by the nature of the heavy masses used, but in the circumstance of time and contact of the insulated screens with the photographic plate not being identical.

Fluorides of Indium and Rubidium.—C. Chabrie and A. Bouchonnet.—The authors prepare the fluorides of indium and rubidium, and examine their properties. The hydrated indium fluoride has the formula $\text{In}_2\text{F}_6 \cdot 18\text{H}_2\text{O}$. It is prepared in the form of white needles, very soluble in cold water and insoluble in alcohol and ether. It emits acid vapours in the air. The rubidium fluoride is produced in very deliquescent crystals.

Union of Diazobenzene and Aniline.—Léo Vignon.—It is known that diazobenzene unites with aniline, and after molecular transposition produces aminoazobenzene, $\text{C}_6\text{H}_5\text{N}_2\text{C}_6\text{H}_4\text{NH}_2$. This azoic amine is diazotable, and apparently gives new derivatives. The author investigates the limit of these reactions, studying chiefly the case of aniline.

Camphene, Camphenylone, Isoborneol, and Camphor.—L. Bouveault and G. Blanc.—The hydrogenation of camphor produces two alcohols which are capable of

regenerating camphor by oxidation: one of these is borneol, identical with the natural product; the second is the substance which was first called unstable borneol and then isoborneol. If camphene is represented by the formula $C_8H_{14} = C = CH_2$, isoborneol is the hydrate of camphene, $C_8H_{14} = C - CH_3$, i.e., the tertiary alcohol,



In accordance with these formulæ, camphenylene would have the formula $C_8H_{14} = CO$.

Diastasic Coagulation of Starch.—J. Wolff and A. Fernbach.—The authors' experiments on the coagulation of starch prove that the state of liquefaction favourable to coagulation is also favourable for the diastasic formation of amylocellulose. The difference between the quantities of amylocellulose which are formed in the absence or presence of diastase is greater in proportion as the starch has, by previous heating, been further removed from its natural state.

Estimation of Carbon Monoxide in Confined Spaces.—Albert Levy and A. Pécoul.—The authors estimate the amount of carbon monoxide in various schools, hospitals, tunnels, &c., in Paris by M. Gautier's method. This method is founded on the reduction of anhydrous iodic acid at a temperature between 60 and 80 and absorption of the iodine by chloroform. The authors find that absolutely all the iodine liberated is retained by the chloroform, the method being therefore quantitative.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxxi., No. 8.

Action of Chlorine on the Anhydrous Acetates.—Albert Colson.—Already noticed.

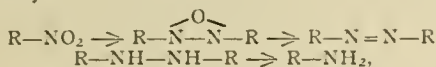
The Phenylurethanes of the Sugars.—L. Maquenne and W. Goodwin.—Already noticed.

Synthesis of Sugars from Trioxymethylene and Sulphite of Soda.—A. Seyewetz and M. Gibello.—Already noticed.

New Syntheses effected by Means of the Molecules containing the Methylene Group Associated with One or Two Negative Radicals. II. Action of Epichlorhydrine on the Acetonedicarboxylic Soda Ethers.—A. Haller and F. March.—Already noticed.

Research on the Azoics. Reduction of Acetals and of Nitrobenzoic Acids.—P. Freundler.—Already noticed.

Research on the Azoics. General Remarks on the Reduction of the Nitro-derivatives in Alkaline Solution.—P. Freundler.—The constant formation of aminised derivatives from the ortho-nitrated compounds appeared to the author to be incompatible with the system of equations, met with in all text-books, to represent the reduction of the nitrated derivatives in alkaline solution. These equations may be summarised as follows:—



The author shows that the bodies with an amine function, which take rise during the reaction in question, are not formed by the reduction of hydrazoics (and consequently by that of azoics or of azoxyques). He also discusses the work done by M. Haber and M. Bamberger on this subject, and, in conclusion, asserts that the aminised derivatives formed during the alkaline reduction of the ortho-substituted nitro-derivatives do not result from a more complete hydration of the hydrazoics, the azoxyques, or the azoics. Therefore they take rise from the reduction of the hydroxylamines.

Some Campholenic Derivatives.—A. Behal.—*Dimethylcampholenol* is prepared by reacting on inactive campholenate of methyl with iodide of methylmagnesium by Grignard's method. *Diethylcampholenol* is prepared in a similar manner, but the iodide of methylmagnesium is replaced with bromide of ethylmagnesium. The author

also describes the preparation and properties of some derivatives of these bodies.

Research on Ricinine.—L. Maquenne and L. Phillippe.—Already noticed.

The Determination of Fusion-points.—L. Maquenne.—Already inserted in full.

Note on Two New Algerian Essences.—P. Jeancard and C. Satie.—These two essences come from the region of the Hauts-Plateaux in Algeria, and were obtained by the distillation of the entire plant. One, the essence of Gouft, is very pale yellow in colour; the other, essence of Scheih, is of a reddish-brown. The latter has an odour similar to that of absinth; the former is more of a turpentine. The physical and chemical constants are given in the form of tables.

MISCELLANEOUS.

The Reciprocal Influence of Dissolved Colloidal Substances.—W. Biltz.—The author has prepared a certain number of colloidal substances, viz., gold, platinum, selenium, sulphides of cadmium, antimony, and arsenic, silica, stannic acid, tungsten and molybdenum blue, vanadic acid, ferric hydrate, alumina, chromic hydrate, hydrate of thorium, zirconia, and ceric hydrate. The first eleven of the above list (negative hydrosols) when submitted to the action of electrolysis go to the anode, while the six last (positive hydrosols) go to the cathode. The author was led to the following conclusions:—1. Hydrosols charged with opposite electricity tend to become precipitated in the form of jelly when they are mixed (in the absence of electrolytes); those which are of the same sign are without mutual interaction; (2) for these precipitations to be complete, it is necessary for the respective quantities of the two colloids to be in a certain proportion (that of equivalence, so-called); if we depart from this condition of equivalence, one way or the other, there is a tendency for the precipitation not to take place. The author calls the products of addition of colloids to other colloids, crystalloids, or to electrolytes, *compounds of adsorption*. Finally, he has examined the simultaneous action of colloids and electrolytes, or the precipitation of other colloids (we know that the influence of the electrolyte increases with the valence of the cation). He finds that the actions of the colloid and of the electrolyte are superposed, and that very often the action that we believe to be due to the electrolyte should in reality be ascribed to the colloid.—*Berichte*, vol. xxxvii., p. 1095.

MEETINGS FOR THE WEEK.

- MONDAY, 13th.—Society of Arts, 8. (Cantor Lecture). "Internal Combustion Engines," by D. Clerk, M.Inst.C.E.
TUESDAY, 14th.—Royal Institution, 5. "The Structure and Life of Animals," by Prof. L. C. Miall, D.Sc., F.R.S.
WEDNESDAY, 15th.—Microscopical, 8. "Practical Micro-metallography" (with Experimental Demonstration), by J. E. Stead, F.R.S.
— Society of Arts, 8. "The Decline of the Country Town," by Arthur Henry Anderson.
— Chemical, 5.30. "Condensation of Amino-acetic Esters in presence of Sodium Alcoholate," by A. T. de Moulpiéd.
— "Nitrogen Halogen Derivatives of the Aliphatic Diamines," by P. D. Chattaway.
THURSDAY, 16th.—Royal Institution, 5. "Recent Work of the Geological Survey," by Prof. J. J. H. Teall, F.R.S., &c.
— Society of Arts, 4.30. "The Indian Census of 1901," by Sir Charles A. Elliott, K.C.S.I., &c.
FRIDAY, 17th.—Royal Institution, 9. "High Power Microscopy," by John W. Gordon.
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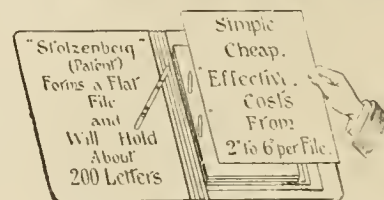
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ON

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THE CHEMICAL NEWS.

VOL. XCI., No. 2360.

ON THE COLOURATION OF GLASS BY NATURAL SOLAR AND OTHER RADIATIONS.*

By Sir WILLIAM CROOKES, D.Sc., F.R.S.

It is well known that many samples of colourless glass containing manganese slowly assume a violet tint when exposed to sunlight. This effect is frequently seen in plate-glass windows having a southern aspect; watched from year to year they assume a more and more pronounced amethystine hue. The introduction of manganese into glass is to neutralise the colour caused by the presence of iron. Iron gives the glass a greenish tint, and the addition of manganese binoxide performs the double object of oxidising the green protosalt of iron to the persalt, and also of imparting a purple shade which neutralises the green-yellow tint of the silicate of peroxide of iron.

In 1903, I received from two separate correspondents specimens of glass coloured an intense purple. I quote the following sentences from the covering letters:—

Mr. A. Ernest Williams writes:—

"While residing at Uyuni in Bolivia last year, at an altitude of nearly 4000 metres, my attention was called to the fact that all transparent white glass when thrown out on the 'Pampa' in a short time assumes a violet hue, which becomes more marked with time. I was told that all specimens were thus affected, and that when taken to sea level at Antofagasta they lost their colour. This latter statement I hardly believe, as I have had some pieces with me now on low level for nearly a year, and they have not lost the colour."

"I now notice that all transparent white glass thrown on rubbish heaps, even at low level, assumes this violet colour, though only to a slight degree, and I am curious to know the cause, being more interested since reading that radium so affects glass."

"I may mention that Uyuni is situated on the great central plain of Bolivia, which plain has evidently formed the bed of an inland sea or lake, for I have found quantities of minute shells there. Not far off to the S. and S.W. are borax fields, and still further west, nitrate. To the N.E. are the mountains of Pulacayo and Cuzco (not the great Cuzco), and electrical disturbances are of almost daily occurrence. I can fully confirm Sir Martin Conway's description of the battles between the mountains, where lateral discharges are plainly visible. I am sending you by post a small specimen of the glass."

About the same time I received some specimens of purple coloured glass from Mr. Thomas Wilson from Iquique, Chile. In a subsequent letter answering some enquiries, he sent a further quantity of the coloured glass, saying:—

"You will notice a great variety in the depth or degree of tint in the different pieces, which may be attributable to the varied length of the exposure of each to the action of the sun's rays. It seems to me that some of the pieces have lost somewhat of their depth of colour since I picked them up, but this may be an impression only. The two pieces forming together the bottom of a broken tumbler, and which have a deeper tint than any of the rest, were found about twenty paces apart in an old Oficina that had been uninhabited for twenty-seven years. It is impossible to give any idea of the length of exposure of the remaining pieces to the sun's rays, as I have obtained them from all parts of the Pampa over an extent of nearly 100 miles.

The samples I send you were originally white glass, and although an abundance of glass of various colours are to be found, yet I send you none, as it would not be easy to say what their original colours had been previous to exposure."

The pieces of glass referred to above are of all depths of tint, from deep violet, almost black in thick pieces, to pale amethyst. Analysis shows the glass to contain manganese. Heating the glass in a covered crucible to its softening point, discharges the colour, leaving the glass white and transparent.

The colouration is not superficial. On immersing a piece of the coloured glass in a liquid of about the same refractive index as itself, the colour is seen to have penetrated throughout the mass.

At first sight the explanation of this phenomenon would seem to be that it is produced by the action of light, the intense radiation occasioning a re-arrangement of the oxygen molecules in the glass, the ferric salt becoming ferrous, and the manganous salt changing to a manganic compound. The change of colour might then be expected to be noticed in any part of the world where broken glass is thrown about and the sun's rays are very intense. In the Transvaal, where both these conditions are well fulfilled, I have neither heard of nor noticed any such colouration, and it would be interesting to hear if travellers in other tropical countries have observed any such change of colour of glass.

Probably height above sea level has much to do with the phenomenon. At a height of 4000 metres nearly half the atmosphere is beneath one's feet, and that which remains will allow rays of shorter wave-length to pass through than the atmosphere at sea level will transmit.

For this reason it is not necessary to invoke another mode of explanation that might possibly suggest itself. It now has been well established that many natural bodies, water from great depths, some samples of earth and rock, air from underground sources, together with some minerals, are more or less radio-active. Radium, acting for a few days, even through quartz, will produce as intense a colouration in a piece of this glass as exposure to the sun on the Pampa has taken years to effect. It is hardly conceivable that there can be a special radio-activity of the soil in certain parts of Chile and Bolivia sufficiently powerful to produce the effect.

A piece of the coloured glass, bleached by heat, was put close to a quartz tube in which about 15 m.grms. of pure radium bromide was sealed up. In the course of a few hours a faint amethystine tint could be distinguished on the glass, and in a week the tint was equal to the deep colour of the unbleached specimen. A duplicate piece of the same glass which had been bleached by heat, kept away from radium, has remained colourless for seven weeks.

A piece of the deepest purple coloured glass was put on a sensitive photographic film, and kept in the dark in contact with it for thirty-four days. No trace of action could be detected on developing.

The purple glass which had been bleached by heat and then coloured purple again by radium, was put in close contact with a sensitive film for twenty-four hours. On developing, no trace of action could be seen.

The darkening effect produced by radium on bodies exposed to its emanations is very general. Quartz, mica, glass of all kinds, and the diamond may be specially mentioned. In a paper recently read before the Royal Society "On the Action of Radium Emanations on Diamond" (*Roy. Soc. Proc.*, June, 1904, vol. lxxiv., p. 47; and *CHEMICAL NEWS*, 1904, vol. xc., p. 1), I showed that the β -rays (electrons) and γ -rays not only effected a superficial darkening, converting the surface of the diamond into graphite, but the body colour of the stone was changed from pale yellowish-brown to bluish-green; and I suggested the explanation that the action might be chemical, the

* A Paper read before the Royal Society, January 26, 1905.

* In this connection it may be of interest to recall the fact that in the early days of photographic research the ultra-violet rays of the spectrum were called the "deoxidising rays."

ferric state of the iron being reduced to the ferrous state, and the colour thereby changing from yellow to blue-green.

In the year 1855, I tried a series of experiments with a spectrum camera furnished with two quartz prisms and a quartz lens, with the object of ascertaining if the atmosphere exerted any absorptive action on the more refrangible rays of light. Photographs of the solar spectrum were found to reveal lines of higher and higher refrangibility the nearer they were taken to mid-day, and arguing from this I concluded that the "noon-day spectrum at midsummer ought to contain more and higher rays than are possessed by the corresponding spectra at any other time of the year." The examination of the photographed spectra was continued through the summer, photographs being taken at noon whenever the sun was clear, and I found that "as the light came less obliquely through the atmosphere, new rays began to be apparent, until at midsummer, when the sun was on the meridian, I succeeded in obtaining evidence of the existence of rays which the most prolonged exposure failed to detect at any other time."

I may perhaps be pardoned for quoting from my paper on the subject the following passage, written fifty years ago (*Journal of the Photographic Society of London*, vol. ii., p. 293):—

"Some curious speculations arise from these facts. Should we be able, by working under a vertical sun, and with every advantage of cloudless sky, &c., to increase still more the length of our spectrum? Can we attain the limit of solar refrangible rays in this direction? Or is it not more likely that there are emanating from the sun torrents of rays which never approach the earth—rays which, beating against the upper stratum of the atmosphere, are themselves destroyed, but whose vibrative energy is transmitted to us with increased wave-length and lowered refrangibility, in the form of heat or light?"

Sunlight and radium both produce similar effects in these respects. Their modes of action are known to be in the main very different; but it has been clearly shown that, in general, variation of time being disregarded, what radium is capable of doing in the way of inducing chemical change, ionising gases, producing phosphorescence, and impressing a photographic plate, sunlight will also effect.

ON THE COMPRESSIBILITY OF GASES BETWEEN ONE ATMOSPHERE AND HALF AN ATMOSPHERE OF PRESSURE.*

By Lord RAYLEIGH, O.M., F.R.S.

THE present memoir contains a detailed account of the observations referred to in the Preliminary Notice of February, 1904 (*CHEMICAL NEWS*, vol. lxxxix., p. 86). In addition, results are now given for air, carbonic anhydride, and nitrous oxide. In the following table are recorded the values of B for the various gases at specified temperatures, B denoting the quotient of the value of p_v at half an atmosphere by the value at the whole atmosphere:—

Gas.	B.	Temperature.
Oxygen	1.00038	11.2
Hydrogen	0.99974	10.7
Nitrogen	1.00015	14.9
Carbonic oxide	1.00026	13.8
Air	1.00023	11.4
Carbon dioxide	1.00279	15.0
Nitrous oxide	1.00327	11.0

By means of a formula given by D. Berthelot the compressibilities at 0° C. are inferred, and applied to deduce the ratio of densities as they would be observed at 0° C. under very low pressures. According to Avogadro's law, these are the relative molecular weights. From the densities of nitrogen and oxygen we get $N=14.008$ if $O=16$. Again, from the densities of oxygen and nitrous oxide we find $N=13.998$. The former is probably the more trustworthy.

* Abstract of a Paper read before the Royal Society, Feb. 2, 1905.

INACTIVE THORIUM.*

By CHAS. BASKERVILLE and FRITZ ZERBAN.

Synopsis.—A new source of inactive thorium has been found in a rock from South America.

Most of the investigators working on radio-activity are of the opinion that thorium is a primarily active body, under all conditions, independently of the source from which it is obtained. K. A. Hofmann, and also the writers, arrived at the assumption that thorium is inactive *per se*, and shows radio-active properties merely under certain circumstances.

One of us investigated Rutherford's thorium-X, especially for its chemical properties (*Journ. Am. Chem. Soc.*, 1904, xxvi., 922). Through the courtesy of the Welsbach Lighting Company he obtained over 100 litres of an ammoniacal filtrate by the extraction of thorium from monazite sand, which is said to contain thorium-X. This liquid, after evaporation and ignition, left a residue showing strong radio-activity, but no trace of thorium could be detected in it. Further, by re-precipitation of a quite chemically pure thorium solution with fumaric acid, according to Metzger's method (*Journ. Am. Chem. Soc.*, 1902, xxiv., 901), evaporation of the filtrate, and ignition, a residue was obtained much more active than the precipitate. These two results can be explained only by the fact that the radio-activity of the common pure thorium preparations is not a property of thorium itself, but of a strange body associated with it.

Now, while it has been found impossible as yet to remove this additional substance thoroughly from thorium, K. A. Hofmann and Zerban did succeed in obtaining entirely inactive thorium directly from mineral sources (*Ber.*, 1903, xxxvi., 3093), but only from such minerals as contain no radio-active bodies at all; for instance, from Norwegian gadolinite, ytrotitanite, and orthite. On the other hand, it has been found that thorium is active only when, but always when, the minerals yielding it contain other radio-active substances.

In these investigations it was also necessary to state the presence of other radio-active bodies than thorium in monazite sand, which was said to contain only thorium as a radio-active body. Indeed, one of us detected very small amounts of uranium in five different samples of monazite sand from various localities (*Ber.*, 1903, xxxvi., 3911). Some time ago Clemens Winkler made some objections to the method used in this work (*Ber.*, 1904, xxxvii., 1655). This matter will be taken up later.

Clemens Winkler also suggested that there are uranium-free monazites, but, in the meantime, Haitinger and Peters have noted the presence of radium in monazite sand. So the radio-activity of thorium from uranium-free minerals may be explained by the presence of radium in them.

In continuing the work on the activity of thorium we analysed a mineral, or more properly speaking a rock, from South America which yielded perfectly and initially inactive thorium. This rock possesses a greyish colour, very similar to common slate.† It consists mostly of barium carbonate, containing a very small percentage of thorium.

Neither the barium nor the thorium in this rock shows any radio-activity. There are no α -radiations given off, and barium within 140, thorium within 290 hours, did not affect the photographic plate through black paper.‡ That our body is really thorium could be proved by the different reactions characteristic for this body. As, first, solubility of the oxalate in a hot solution of ammonium oxalate and re-precipitation of the oxalate after diluting and cooling:

* Read before the New York Section of the American Chemical Society, and published by permission of the Carnegie Institution. From the *Journal of the American Chemical Society*, xxvi., No. 12.

† We are indebted to Dr. Geo. C. Lee, of Philadelphia, for the material.

‡ Even after an exposure of 600 hours no effect upon the plate can be noted, as two subsequent experiments show.

second, by precipitation with sodium thiosulphate, potassium iodate, fumaric acid, *m*-nitrobenzoic acid, and phenylhydrazine. The quantity of the body obtained was very small, so that we could not carry out a determination of the atomic weight. We are now occupied, however, in working with larger quantities of the rock, and hope to be able soon to determine whether or not this new variety of thorium is of a simple elementary nature or capable of being resolved into the three constituents, berzelium, carolinium, and new thorium.

The important bearing these observations have on the very recent theories of radio-activity is apparent.

"BERYLLIUM" OR "GLUCINUM."

By CHARLES LATHROP PARSONS.

SINCE the Council of the American Chemical Society has requested the smaller International Committee on Atomic Weights to submit the question of choice between the two names "beryllium" and "glucinum" to the whole or larger committee in order that uniformity of usage may be secured, it is evident that a considerable difference of opinion exists among American chemists as to the advisability of adopting the latter name.

The question is one of decided importance in indexing our chemical literature, and as I have had this matter brought continually to my attention during the preparation of a bibliography of the element, now complete in card form, I should like to present the very strong reasons for the universal use of "beryllium," at least as they appear to me. These reasons are two, and may be summarised as (1) priority and (2) usage.

Priority.—It has been generally supposed by chemists who have not carefully looked into the matter that the name "glucinum," or at least "glucine," originated with Vauquelin, the discoverer of the element, but this is not the case. In fact, a distinction should be made between the terms "glucinum" and "glucine," for the former first came into use many years afterward when the metal itself was obtained, and the real claim for priority must be a question between "glucine" and "berylerde," from which the others were derived.

Vauquelin himself uses the clause "la terre du Béril" exclusively in his first two articles on the subject in speaking of the new oxide he had discovered (*Annales de Chim.*, xxvi., 155, and xxvi., 170). The term "glucine" was proposed by the then editors of the *Annales*, Guyton and Fourcroy, in a note at the end of Vauquelin's first article, and signed simply "Redacteur." Vauquelin evidently presented his results for the second time to the French Society of Mines, for they again appear in the *Journal des Mines*, viii., 553. Here also Vauquelin uses only the clause "la terre du Béril," but gives support to the term "glucine" by a note at the end of his article as follows:—"La propriété la plus caractéristique de cette terre étant de former du sels d'une saveur sucrée, les Cens. Guyton et Fourcroy m'ont conseillé de lui donne le nom de glucine de ($\gamma\lambda\upsilon\kappa\eta\varsigma$), doux. Cette denomination sera assez significative pour aider le mémoire; elle ne prendra pas dans son étymologie un sens trop strictement déterminé, et ne présentera pas d'idées fausement exclusive, comme celles que l'on tire du nom de la pierre qui fourni le premier échantillon de la substance nouvelle, &c."

Vauquelin's adoption of "glucine" appears from the character of the argument he puts forth to be at least half hearted. He first actually employs "glucine" in his third article, entitled "Analyse de l'émeraude du Péron" (*Annales de Chim.*, xxvi., 259), prefacing its use with "on a donné le nom de glucine."

The clause "la terre du Béril" was translated into German as "berylerde" in the reprints of Vauquelin's articles, and became the name used thereafter by all of the German and

Swedish chemists who did much the larger portion of the work of developing the chemistry of the element.

Usage.—If "use is the law of language" then the supporters of "glucinum" have little upon which to base their argument. By far the larger number of investigators of the element and its compounds have used and are using "beryllium." All the leading chemical journals of the world with the exception of those in the French language give preference to the latter term, and in most cases use it exclusively. The German, Swedish, and Dutch chemists who have the greater number of original articles to their credit use no other. Italians use "berillio" from the same root. English journals until recently used the name preferred by the particular author, but they have now almost ceased to put even the "glucinum, see beryllium" in their indexes.

For American chemists to attempt to bring the world to the use of "glucinum" when by far the majority of chemical journals have dropped it even as a synonym is, in my opinion, worse than useless, even if there was a preponderance of argument in its favour.—*Science*, Dec. 9th, 1904.

THE HYDRATES OF MOLYBDIC ACID.

By ARTHUR ROSENHEIM and ISSER DAVIDSOHN.

YELLOW molybdic acid—that is to say, the dihydrated acid—is precipitated almost quantitatively by the addition of nitric acid and nitrate of ammonia to alkaline solutions of molybdates. Precipitation is slow, which leads us to the opinion that the dihydrate does not correspond to $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$, but to a condensed form, $(\text{MoO}_2 \cdot 2\text{H}_2\text{O})_n$.

The solutions of the dihydrate behave in the same manner as strong electrolytes, and contain an acid of the composition $\text{H}_{2x}[(\text{MoO}_3)_4]_y\text{O}_x$, probably $\text{Mo}_5\text{O}_{25}\text{H}_2$.

By treating the dihydrate with methylic alcohol we obtain a dimethylmolybdate having the simple formula $\text{MoO}_4(\text{CH}_3)_2$. Thus methylic alcohol behaves, with regard to the yellow polymeric dihydrate, exactly like the alkalis. In aqueous solution it is hydrolysed into hydrated molybdic acid and alcohol. The aqueous solution of this hydrate is less easily dissociated than that of the dihydrate.

On heating solutions of the dihydrate to about 40–50°, we obtain a well crystallised white monohydrate (the α -hydrate) having a very different solubility to that of the dihydrate. Its solutions also behave differently from those of the dihydrate. The conductivity of its solutions, for example, is almost the same as that of the molybdate of methyl, which brings us to the conclusion that this α -monohydrate may have a rather low molecular weight, apparently corresponding to the formula $\text{MoO}_3 \cdot \text{H}_2\text{O}$.

By heating the solutions of the dihydrate to 60–70°, we obtain a new variety of the monohydrate (the β -variety). This form is identical with that obtained by the action of heat on the dihydrate held in suspension in water at 70°. It is distinguished very easily from the α -monohydrate by its crystalline form and its easy dehydration.

The examination of the reciprocal transformation of the two hydrates, one into the other, shows that it is a complex phenomenon, as we find ourselves face to face with the simultaneous phenomena of hydration and of polymerisation, which is only effected slowly.

Colloidal solutions of molybdic acid are obtained by the dilution of the solutions of the dihydrate at 20°, or better still, by the action of heat on solutions of $\text{MoO}_3 \cdot \text{Na}_2 + 4\text{HCl}$ at 45°. The hydrosol obtained is easily soluble, and is precipitated from its solutions by electrolytes. Graham's method of preparation does not give a colloidal acid.

The solubility of the dihydrate in water is slight; in the presence of sulphate of ammonia its solubility is considerably increased. The α -monohydrate only loses 1.46 per cent of water at 120°; the β -hydrate loses 11.54 per cent. The solubility of the α -monohydrate, at temperatures

below 30° , is superior to that of the dihydrate; the curves of solubility cross at 32° .

The curve of the α -monohydrate shows an anomaly in the neighbourhood of 60° (viz., minimal solubility), and it is probable that this particularity of the curve corresponds in the solution with the transformation of the α - into the β -salt, $\text{Mo}_{10}\text{O}_{31}\text{Na}_2 + 7\text{H}_2\text{O}$ or $\text{Mo}_{12}\text{O}_{37}\text{Na}_2 + 8\text{H}_2\text{O}$. This salt is formed by the solution of molybdate of soda in hydrochloric acid.—*Zeit. Anorg. Chem.*, vol. xxxvii., p. 314.

ON GERANIUM CHLOROPHYLL.

By A. B. GRIFFITHS, Ph.D., &c.

THE green pigment known as "chlorophyll" occurs in all plants except the fungi, and is frequently associated with other pigments which may mask it, or may replace it in special parts of the plants. The chief pigment associated with chlorophyll is xanthophyll (a yellow lipochrome), and the mixing of these two pigments in different proportions gives most of the various tints or shades of leaves. There may be many other pigments (lipochromes and non-lipochromes) associated with chlorophyll, but the function of xanthophyll, and probably of other pigments, is unknown. It may be that they protect the protoplasm from the injurious effect of certain rays of white light by absorbing them, or that they assist in the process of assimilation, or that they are instrumental in the polymerisation of formaldehyde and its conversion into starch. Chlorophyll, according to the investigations of the older workers, is stated to be a mixture of phylloxanthin (yellow) and phyllocyanin (blue). Schunck stated that acids transform "leaf-green" into phyllocyanin and phylloxanthin; that alkalis and strong acids convert phyllocyanin into phyllo-taonin ($\text{C}_{40}\text{H}_{40}\text{N}_6\text{O}_6$); that alkalis convert "leaf-green" into alka-chlorophyll ($\text{C}_{52}\text{H}_{57}\text{N}_7\text{O}_7$), which, on treatment with acids and alcohol, yields an alkylether of phyllo-taonin; and that on heating phyllo-taonin with alcoholic potash, phylloporphyrin ($\text{C}_{32}\text{H}_{34}\text{N}_4\text{O}_2$) is obtained.

From the important researches of Gautier, Etard, and others there appear to be several chlorophylls,* and there is little doubt that many chlorophylls exist in nature. It is no argument to say that because chlorophyll is a green pigment, and that it appears to perform a definite function, there can be only one which is homogeneous, or one composed of xanthophyll and cyanophyll; we might just as well say that because there are yellow and red chromophylls in the petals of flowers they are identical in composition (even their spectra differ considerably).

Etard (*Comptes Rendus*, cxx.) has isolated α -medicagophyll ($\text{C}_{28}\text{H}_{45}\text{NO}_4$) and β -medicagophyll ($\text{C}_{42}\text{H}_{63}\text{NO}_4$), from lucern (*Medicago sativa*); Gautier has isolated a crystallised chlorophyll from spinach (spinach-chlorophyll, $\text{C}_{40}\text{H}_{64}\text{N}_2\text{O}_4$), and Hoppe-Seyler extracted another from grass (grass-chlorophyll, $\text{C}_{30}\text{H}_{46}\text{N}_2\text{O}_3$). Etard (*Ann. Inst. Pasteur*, xiii., p. 456) has isolated three aspidiophylls from ferns ($\text{C}_{208}\text{H}_{347}\text{NO}_{32}$, $\text{C}_{240}\text{H}_{320}\text{N}_2\text{O}_{31}$, and $\text{C}_{210}\text{H}_{346}\text{N}_{20}\text{O}_{48}$). The chlorophylls from ferns are complex or large molecules (Griffiths, "Respiratory Proteids," L. Reeve and Co.).

The latest investigations tend to prove that other chlorophylls or chloroglobins exist in the vegetable. For the present it may be stated that I have spectroscopically studied geranium-chlorophyll extracted by neutral solvents from the leaves.

This proteid has not yet been subjected to analysis, its chemical composition is therefore unknown, but several peculiarities have been carefully recorded, and especially the effect of oxidising and reducing agents, &c., upon solutions of it in alcohol. It dissolves readily in alcohol, by means of which it was extracted. The spectrum of the solution of geranium-chlorophyll showed absorption bands in the red and most of the orange; in two places in the

green, and in the blue, the dark part of which was entirely obliterated, while the light portion was still faintly visible.

The solid chlorophyll may be obtained from this solution by careful evaporation, and subsequently treating the residue with ether and filtering. The purified chlorophyll, which is only slightly soluble in ether, was freed from fat and other substances. A solution of the purified chlorophyll was made in alcohol, and 25 per cent of a solution of sodium hydroxide was added, when a green substance was precipitated, and the solution became cloudy. This green precipitate is very stable, and when re-dissolved it gave a characteristic spectrum (a band from H to beyond F, and another one at E); and the alkaline filtrate, already referred to, also gave a particular absorption (from A to a and a to C, and E to H₁).

Ammonium sulphide precipitates almost identically the same green substance having almost the same spectrum—absorption band beyond A (deep red), one at E, and one from F to H₁. The filtered solution after the addition of the sulphide alters the spectrum of the pure ammonium sulphide (absorption from beyond F to H₁) by making an absorption which was intense in the blue, rather feeble, and by adding a new band in the light green.

When hydrogen dioxide (20 volume solution) was added a similar green precipitate was thrown down, but only slightly, and the filtered solution gave a spectrum resembling the last one mentioned with a deep band in the green replaced by a feeble one.

When reduced by means of nascent hydrogen generated in the solutions by means of zinc and hydrochloric acid, a green substance was feebly precipitated, and the solution, when filtered, gave an absorption band from G to H₁, a feeble band from b to d, and small bands on either side of D.

When iodine water was added to a solution of geranium-chlorophyll, a peculiar result was obtained. The otherwise unbroken band of absorption shown by pure iodine water, which extends from the ultra-violet right across the D line of the solar spectrum, was rendered transparent just round the E and b lines, and was totally eliminated at a thin line in the D position, where yellow showed through very distinctly.

Geranium-chlorophyll is only slightly soluble in ether, and when extracted by it the faint green solution showed a band just covering the blue, and a narrow band in the deep red; thus differing totally from the solution in alcohol.

Aniline oil was also used as a solvent, but it did not extract any geranium-chlorophyll—in fact, it is insoluble in aniline.

I am of opinion that the chlorophyll present in the leaves of geranium is a distinct proteid; and there is a certain amount of proof that the chlorophylls are *albumenoids*. Schunck and Marchlewski (*Proc. Roy. Soc.*, vol. lix., p. 234) have shown that chlorophyll can be made to yield pyrrol ($\text{C}_4\text{H}_5\text{NH}$). It is also well known that indigo is a derivative of indol, the pyrrol of the aromatic or benzene series, and that indol [$\text{C}_6\text{H}_4(\text{CH})_2\text{NH}$] may be obtained by the pancreatic decomposition of *albumenoids*, and by the fusion of the latter with potassium hydroxide.

Chemical Society Anniversary Dinner.—It has been decided by the Council to arrange for a Dinner of the Fellows of the Society and their friends on Wednesday, March 29th, 1905, this being the day fixed for the Annual General Meeting. Further particulars will be announced shortly.

Colloidal Hydrate of Iron obtained by Electro-dialysis.—J. Tribot and H. Chrétien.—It is known that when a solution of ferric chloride is subjected to dialysis in presence of ferric hydrate, at the end of a definite time a colloidal iron hydrate is formed, which always retains a certain quantity of chlorine. The authors now endeavour, by using an electric current, to reduce the amount of chlorine, and they are able to prove that the current, when used with Graham's apparatus, does facilitate the separation of the chlorine. They are continuing their researches on this subject.—*Comptes Rendus*, cxl., No. 3.

* There are many chromophylls (chromoplasts).

ON SOME CUPRAMMONIUM SULPHATES.*

By DAVID W. HORN and EDYTHA E. TAYLOR.

(Continued from p. 68).

II. Preparation of the Salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$
(continued).

B. Mallaert's Method.—The method suggested by Mallaert (*Journ. de Pharm. d'Anvers*, 1848, 217; *Svanberg's Fähsb.*, 1851, xxx., 119) for the preparation of the salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ consists in the action of ammonia gas on solid $\text{CuSO}_4 + 5\text{H}_2\text{O}$. We observed a very rapid change to purple colour when finely ground copper sulphate was put in a desiccator over ammonia water. This promised to be a convenient method for the preparation of the salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$, provided the purple product is of this composition.

"Pure" copper sulphate was re-crystallised five times from water, and its purity assured by the following analyses of the (air-dried) product:—

Weight of salt taken for analysis.	Weight of copper found.	Percentage of copper found.	Percentage of copper calculated for $\text{CuSO}_4 + 5\text{H}_2\text{O}$.
Grm.	Grm.		
0.4404	0.1121	25.47	25.47
0.4267	0.1087	25.47	
0.3598	0.0915	25.44	

Specimens of this salt were weighed into porcelain boats and the boats put into glass tubes in a current of air that had first bubbled through ammonia water (sp. gr. 0.09). The boats were frequently transferred rapidly to well-ground glass-stoppered weighing-tubes and weighed. The following were the results:—

Time in minutes.	Weight of specimen.		Changes in weight.	
	I.	II.	I.	II.
	Grms.	Grms.	Grm.	Grm.
0	2.0622	1.5436	—	—
15	2.3575	1.8485	+0.2953	+0.3049
40	2.4628	1.8994	+0.1053	+0.0509
55	—	1.9035	—	+0.0041
60	2.5170	—	+0.0442	—
85	2.5261	1.8912	+0.0091	-0.0123
105	2.5238	—	-0.0023	—
135	2.4911 (T)	—	-0.0327	—
150	—	1.8608 (T)	—	-0.0304

The weighings were continued for half a day longer, and showed continued losses. At the end of that time the specimens were about 0.3 grm. heavier than the original $\text{CuSO}_4 + 5\text{H}_2\text{O}$. The above figures show maxima corresponding to gains in weight of 22.5 and 23.2 per cent respectively. A gain of 24 per cent would represent the addition of 3 molecules of ammonia to each molecule of $\text{CuSO}_4 + 5\text{H}_2\text{O}$. Such addition-products have been described, especially in connection with the action of hydrochloric acid on copper sulphate (Latschinoff, *Journ. Russ. Phys. Chem. Soc.*, 1888, pp. 586, 657, 707; *Fähsb.*, 1888, i., 621; 1889, i., 517); for example, $\text{CuSO}_4 + 5\text{H}_2\text{O} + 3\text{HCl}$.

Whatever may be the case in other instances, the products here are mixtures, as was clearly shown by the mixed colours of the contents of the boats after drying over lime. The colours ranged from sky-blue to purple. The action by which the coloured mixtures are produced is accompanied by considerable evolution of heat.

To avoid the mechanical retention of much water on the surface of the salt (as was the case in the glazed porcelain boats), and to allow sufficient time for the action to complete itself, pure copper sulphate was next placed on an unglazed porcelain plate in a desiccator containing ammonia water (sp. gr. 0.9). The following analyses for am-

monia were made of specimens that were dried over lime after removal from the desiccator containing ammonia water. I. was a specimen taken after three days, and II. was a specimen taken after four months:—

	Weight of salt taken for analysis.	Weight of ammonia found.	Percentage of ammonia found.	Percentage of ammonia calculated for $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$.
	Grm.	Grm.		
I.	0.3577	0.0962	26.93	27.75
II.	0.4305	0.1191	27.70	
	0.4591	0.1278	27.82	

From the analyses of II. it might be inferred that the final product of the action of ammonia gas on pentahydrated copper sulphate is $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$, as was stated by Mallaert. This was disproved in two ways:—First, by the analyses of II. for copper; and second, by the fact that II. was not completely soluble in water, but left a green insoluble residue. The analyses for copper resulted as follows:—

Weight of salt taken for analysis.	Weight of copper found.	Percentage of copper found.	Percentage of copper calculated for $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$.
Grm.	Grm.		
0.2945	0.0769	26.13	25.87
0.3227	0.0843	26.13	

We conclude that the product of the action of ammonia gas on pentahydrated copper sulphate is not the salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$, as stated by Mallaert, and as indicated by the percentage of ammonia found in the final product, but that it is a mixture containing basic salts or copper oxide.

C. Andrae's Method.—Andrae (*Comptes Rendus*, c., 1138) has stated that when ammonia gas is passed into a solution of copper sulphate fine crystals of the salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ separate out as the concentration of ammonia in the liquid rises. Analyses are not given in Andrae's paper. This method, by which the solid is produced gradually and in fine crystals, is, in our opinion, the best for the preparation of the pure salt.

We prepared several hundred grms. of the salt by this method and dried it over lime. We then made a complete analysis of it, and have used it as the basis for the rest of our work. The following results were obtained in its analysis:—

Con-	Weight of	Weight of	Percentage of	Percentage
stituent	salt taken for	constituent	constituent	calculated for
determined.	analysis.	found.	found.	$\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$.
	Grm.	Grm.		
Cu	0.3543	0.0916	25.86	25.86
	0.4790	0.1239	25.87	
	0.5120	0.1325	25.88	
	0.4907	0.1268	25.84	
SO ₄	0.3378	0.1324	39.19 (T)*	39.06
	0.2631	0.1026	39.00 (T)	
	0.3100	0.1212	39.09 (T)	
	0.3383	0.1322	39.08 (T)	
NH ₃	0.4419	0.1220	27.61 (T)	27.75
	0.3927	0.1092	27.80 (T)	
	0.5358	0.1488	27.77 (T)	
	0.3833	0.1067	27.84 (T)	
H ₂ O	0.6691	0.0494	7.38†	7.33
	0.5701	0.0417	7.31	
	1.2860	0.0944	7.34	
	0.5967	0.0438	7.34	

* Determined by method described on p. 52.

† Determined by method described on p. 51.

Specimens taken from this quantity of salt were used in all of the subsequent experiments involving $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ described in this paper.

* From the *American Chemical Journal*, xxxii., No. 3.

III. *Properties of the Salt* $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$.

The dry salt is odourless. However, ammonia is given off by it instantly when it is moistened, and very soon when it is exposed to the air. It is perfectly stable when kept in a closed space over lime, as is proven by the following analyses of a specimen taken from that quantity, the complete analysis of which has just been given. This specimen had been kept over lime one year:—

Con- stituent determined.	Weight of salt taken for analysis. Grm.	Weight of constituent found. Grm.	Percentage of constituent found.	Percentage calculated for $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$.
Cu	0.4102	0.1060	25.85	25.86
	0.5012	0.1297	25.87	
	0.5209	0.1348	25.88	
NH ₃	0.4766	0.1322	27.74	27.75
	0.5006	0.1393	27.82	
	0.3806	0.1057	27.77	

The dry salt is not stable in a vacuum over concentrated sulphuric acid, as is shown by the following weighings of a finely ground specimen of it that was treated in this way:—

	Grm.
Original weight	0.4371
Weight after twenty-four hours	0.4355
Weight after fifty-two hours	0.4328
Weight after three hundred and six- teen hours	0.4144

The salt dissolves readily in small quantities of water, giving perfectly clear solutions. Its solubility in water between 21° and 22° C. was determined by sealing a quantity of the salt in a glass tube with a quantity of water that was not sufficient to dissolve it, and shaking the tube four hours. The contents of the tube were centrifuged after the shaking was complete and before the tube was opened. Two weighed quantities of the clear liquid then taken from above the crystals in the tube, by means of a pipette, were evaporated to dryness and analysed for copper. The results were as follows:—

Weight of solution analysed. Grms.	Weight of Cu ₂ S found. Grm.	Weight of Cu ₂ S yielded by 1 grm. of solution.
2.2723	0.2252	0.0991
1.4955	0.1481	0.0990

The corresponding weight of the salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ that was dissolved by 100 grms. of water at 21° to 22° C. was 18.05 grms.

The salt takes up ammonia in a desiccator over sticks of potassium hydroxide and a very little ammonia water. This has been proven already on page 68. In this first experiment, however, the analyses were made after the salt had been exposed thus for only about two weeks. Latschinoff has stated that the molecule of water in the salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ is replaced by a molecule of ammonia in an atmosphere of dry ammonia. In another experiment, therefore, we kept this salt over sticks of potassium hydroxide and a few drops of concentrated ammonia water for four months before the following analyses of the resulting product were made:—

Con- stituent determined.	Weight of salt taken for analysis. Grm.	Weight of constituent found. Grm.	Percentage of constituent found.	Percentage calculated for $\text{CuSO}_4 + 5\text{NH}_3$.
NH ₃	0.4513	0.1558	34.52	34.83
	0.3517	0.1217	34.59	
Cu	0.3638	0.0946	26.01	25.97
	0.4145	0.1079	26.02	

The salt had not lost its crystalline form in the four months. Its colour had become less purple (bluer) than it was originally.

The analyses show that, under the stated conditions ammonia had entered the molecule of the salt in the place of water; they show, in addition to this, however, that the reaction is not a clean one, resulting in the formation of the compound $\text{CuSO}_4 + 5\text{NH}_3$, but one giving rise to mixed products containing basic salts or copper oxide.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Extra Meeting Wednesday, January 25th, 1905.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

Prof. W. H. PERKIN, F.R.S., delivered the Wislicenus Memorial Lecture.

Prof. PERCY FRANKLAND, in proposing a vote of thanks, said:—

"As a pupil of the late Professor Wislicenus, it has afforded me the greatest pleasure to listen to the admirable discourse of my friend Professor Perkin on the life-work of the great master to whom both he and I look back with reverence and affection, and to whom we both, and indeed all his pupils, of whom there are several others in the room to-night, owe so much and in such a variety of ways.

As one who, perhaps more than any of his other English students, enjoyed the privilege of his personal friendship and confidence, connected as I was with him by family ties, I may perhaps be permitted to add a few words with regard to Wislicenus as a man.

His work and reputation as an investigator will last as long as the present era of civilisation continues, for in the classical publications of which he is the author he has built up for himself a monument more enduring than brass or marble; but there is risk that the knowledge of many of the rare gifts with which he was so liberally endowed may pass away with the generation that knew him. The commanding presence and those regular features, which might have well served Phidias or Praxiteles as a model for the Olympian Zeus, can, and will, be handed down in the portraits of him which are extant, but not so that magnetic oratory which clothed with romantic charm even the driest details of our science, nor the sympathetic flash of his penetrating eye and the kindly geniality of his smile, for these are things which can live only in the memories of those who had the privilege of his acquaintance in the flesh.

All through life Wislicenus was destined to be a leader of men. Already at school, as you have heard, he excelled all other boys in physical exercises—in swimming and gymnastics, in natural science, and especially in his command of the German language. When trouble came upon his father's house, you have heard how the conduct of his family into exile in America devolved upon him, although he was but eighteen years of age at the time. On the way to America, when cholera broke out on the ship, we find him taking charge of the steerage passengers stricken with the disease, and who had been abandoned by the doctor, not because the latter was overwhelmed with the necessities of the saloon passengers, as charitably asserted by Professor Perkin, but in reality because the doctor was devoting his attention to the whisky bottle in his own cabin. Arrived in America we find him supporting the family out of his slender earnings when he was still in his apprenticeship. On his return to Europe we find him rapidly promoted to the highest position in the academic world of Switzerland. At Würzburg he twice occupied the honourable position of Rector Magnificus of the University, and on the second occasion he was specially selected as, of all the professors, obviously the one most fitted to preside over the festivities

connected with the tercentenary Jubilee of the University. On his transference to Leipzig we find him again soon filling the office of Rector of that University.

But it was not only in academic matters that he was marked out for leadership and distinction, for in any emergency, whether in private or public life, his friends and colleagues turned to him for support and counsel. This is well illustrated by an incident which occurred in Zürich at the close of the Franco-German war. The German inhabitants were celebrating the declaration of peace by means of a 'Commerz' in the Tonhalle, and had thereby so excited the hostility of the Swiss, who were violently pro-French in their sympathies, that an angry crowd gathered outside, commenced throwing stones, and ultimately, I regret to say at the instigation of an English student, set fire to the building. The situation inside had had now become very serious, the staircase was in flames, and no water was procurable. Under these circumstances Wislicenus, who was presiding over the assembly, conceived the idea as original as it was effective of having a cask of beer brought up from the cellar, and, after placing it in a suitable position, ordered it to be broken to pieces, with the result that the escaping beer extinguished the fire. When the company then left the building with Wislicenus at their head, his majestic figure, suggestive of a mediæval knight '*sans peur et sans reproche*,' silenced the hooting multitude, which until his appearance in their midst had been quite prepared to stone the Germans, and even to burn them alive.

In politics Wislicenus was also a great power, especially in the later years of his life. He was one of the founders of the 'Alldeutscher Verband' or Pan-Germanic Confederation, and he was the originator of the idea of greatly increasing the strength of the German Navy.

If I am not trespassing too much on your time I should like to relate a story told me by Wislicenus about one of his experiences in America, and which throws an interesting light on the state of professional chemistry in that country during the 'fifties of the last century. One day he was visited in his laboratory by two American gentlemen, who requested him to analyse and report on a sample of water from a mineral spring which they wished to boom for its therapeutic properties. They said they must have the analysis and report by the afternoon of the same day. This, Wislicenus said, was quite impossible, as the analysis would certainly take several days, and possibly even longer. The gentlemen replied that they were of course prepared to pay him double the usual fee, provided that the results of analysis were in their hands by the afternoon. Their surprise was unbounded when he still remained obdurate, and, saying that they guessed he must be a young greenhorn, they went to another chemist of high repute in the city, who duly furnished them with an elaborate analysis and report on the same day. This chemist afterwards cynically told Wislicenus that he had, to meet the exigency of the case, devised a method of analysing water by smell! In this atmosphere, Wislicenus began to feel exercised as to his moral security, or, to use his own words, '*ich fühlte mich dort nicht gewahr*,' and resolved to return to Europe at the earliest possible opportunity.

But Wislicenus exhibited the same high principle in all his dealings, and carried his lofty idealism and undivided devotion to duty into the smallest details of life, and these aspirations he had the power of communicating to those with whom he came in contact. Without any touch of Puritanism in the ordinary sense of the word, for he was full of good fellowship and the friend of conviviality, he was one of those men who purify all their surroundings. In his presence it was impossible for anyone to harbour a mean or unworthy thought; his searching but optimistic gaze irresistibly drew forth the good and cast out the evil. I was also by means of this unquenchable optimism, let us call it Faith, *der unerschütterliche Glaube*, that he was able to bear with such marvellous fortitude and resignation the terrible domestic afflictions with which his home was

repeatedly visited, and which were calculated to embitter or even drive to despair any weaker nature, but which served to impress the spectator of Wislicenus's troubles with awe and reverence for the absolute fearlessness and self-command of the man. Indeed, I have always felt that to him might well be applied the lines of Horace descriptive of the unswerving heroism of the stoic:—

*'Si fractus illabatur orbis;
Impavidum ferient ruinae.'*

Prof. ARMSTRONG seconded the motion, which was supported by Dr. L. T. THORNE, who said:—

"As another old pupil of Professor Wislicenus, I wish warmly to support the vote of thanks proposed to Professor Perkin for the admirable memorial lecture he has just given, and also to add my own word of homage and gratitude to the memory of our old and loved master. I had the privilege not only of being one of Wislicenus's pupils, but also of being for some time his lecture assistant, and, as such, of living under the same roof with him, and therefore of seeing much of his family life. I can fully confirm the vivid picture of the strong, noble, and kindly nature of the man which has been given by the lecturer. Wislicenus knew, and was interested in, the work of all his students, even the most elementary. To his advanced students engaged in research work he was not only the teacher, but also the friend and fellow-worker in his beloved science, and his own love for and enthusiasm in chemical research roused a similar feeling in his pupils. At the meetings of the Würzburg Chemical Society, which he founded, he was not so much the master as the fellow-student, and these meetings were most helpful, and are still a pleasant memory with all old pupils.

All will read with the greatest interest the review of Wislicenus's work given by the lecturer, work which has been of such value to chemistry in general, and to the question of the atomic configuration in space in particular. Although, as Professor Perkin has said, not many papers dealing directly with this latter subject appeared during Wislicenus's professorship at Würzburg, I can testify that the interest in this question largely underlay the work of Wislicenus and his pupils during that period. Much of the work on the derivatives of ethyl acetoacetate was undertaken in the hope that, by modifying the conditions of replacement, substances showing optical activity might be artificially built up, and thus help to prove the asymmetrical theory; and although negative results always ensued, Wislicenus's interest in the question did not diminish.

Personally, I have always felt that Wislicenus's strong personality and friendly and even fatherly interest had a great influence on my life, an influence which I acknowledge with gratitude, and I believe the same feeling is entertained by all other old pupils. Wislicenus's life and work has undoubtedly done much for the good of chemistry."

The vote of thanks to the lecturer was then carried unanimously.

Ordinary Meeting, Thursday, February 2nd, 1905.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

MESSRS. Percy E. Spielmann and Alfred F. Joseph were formally admitted Fellows of the Society.

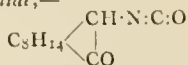
Certificates were read for the first time in favour of Messrs. Bernard Scott Evans, B.Sc., 81, Babington Road, Streatham, S.W.; John Greig Ferrier, 2, Dalhousie Place, Arbroath, N.B.; Archibald Melville Glass, B.Sc., 73, Roderick Road, Hampstead, N.W.; Samuel Ernest Groves, 10, Melrose Avenue, Monkseaton; Peter Maguire, Hamer House, Rochdale, Lancs.; Ernest Robert Marle, B.Sc., 135, Le Marchant Road, St. John's, Newfoundland; Charles Stuart Shepherd, Worth Matravers Vicarage, Wareham; William Ewart Speight, Corporation Sewage

Works, Deighton, Huddersfield; Arthur Walsh Titherley, D.Sc., Ph.D., Southcot, Moreton, near Birkenhead.

Of the following papers, those marked * were read:—

*12. "Camphorylcarbamide." By MARTIN ONSLOW FORSTER and HANS EDUARD FIERZ.

Camphorylcarbamide,—

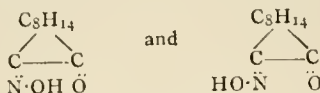


melting at 77°, is readily volatile in steam, and the vapour has a stupefying odour; it is quickly changed by water to dicamphorylcarbamide, $\text{CO}(\text{NH}\cdot\text{C}_{10}\text{H}_{15}\text{O})_2$, which melts at 261°, and, with organic bases, yields symmetrical disubstituted carbamides; for example, camphorylpiperidylcarbamide, $\text{CO}(\text{NC}_5\text{H}_{10})\cdot\text{NH}\cdot\text{C}_{10}\text{H}_{15}\text{O}$, and camphorylbornylcarbamide, $\text{CO}(\text{NH}\cdot\text{C}_{10}\text{H}_{17})\cdot\text{NH}\cdot\text{C}_{10}\text{H}_{15}\text{O}$, which melt at 186° and 305° respectively.

In addition to Rupe's camphorylcarbamide, from which camphorylcarbamide is obtained by the action of nitrous acid, aminocamphor hydrochloride, and potassium cyanate yield camphoryl-ψ-carbamide, $\text{C}_{11}\text{H}_{18}\text{O}_2\text{N}_2$, which melts and decomposes at 188°; the nitroso-derivative, $\text{C}_{11}\text{H}_{17}\text{O}_3\text{N}_3$, which is not obtainable from the normal compound, melts at 158°, and, when freshly prepared, yields camphorylcarbamide with boiling water, losing this property in the desiccator. Camphorylmethyl-ψ-carbamide, $\text{C}_{12}\text{H}_{22}\text{O}_2\text{N}_2$, the corresponding substance from methylaminocamphor, melts and decomposes at 200°; it is indifferent towards nitrous acid, and develops an intense malachite-green colour with concentrated sulphuric acid.

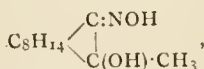
*13. "Configuration of isoNitrosocamphor and its Unstable Modification." By MARTIN ONSLOW FORSTER.

It now seems possible to represent isonitrosocamphor and its unstable form by the configurations—



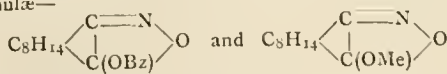
syn-Modification; m. p. 152°. anti-Modification; m. p. 114°.

respectively. The evidence which, taken in conjunction with previous observations, has led to this conclusion arises from the behaviour of the isomerides towards magnesium methyl iodide. Of the four oximes,—



theoretically obtainable, three have been isolated, and melt at 178°, 183°, and 187° respectively; these compounds are amphoteric, and solutions of all three in dilute sulphuric acid yield the liquid anhydride, $\text{C}_{11}\text{H}_{17}\text{ON}$, when warmed. Only two are transformed in warm alkali, however, the α-oxime (m. p. 178°) resisting this treatment; as the α-oxime is derived from the unstable isonitrosocamphor (m. p. 114°), the latter appears to have the anti-configuration.

This conclusion receives support from the behaviour of the colourless benzoyl derivative and the O-methyl ether of isonitrosocamphor, which are now represented by the formulæ—



respectively. This type of structure explains the production of α-camphornitrilic acid on hydrolysis, and the conversion into α-aminocamphor on reduction; moreover, magnesium methyl iodide transforms the above compounds into dimethylaminocamphor, the yield of which is quantitative in the case of the colourless benzoyl derivative.

*14. "The Determination of Molecular Weight by Lowering of Vapour-pressure." By EDGAR PHILIP PERMAN.

The author has worked out the details of a simple method by which molecular weights can be determined with moderate accuracy from measurements of the lowering of vapour-pressure of the solvent in which the substance under investigation is dissolved. The solution is heated in the vapour of the pure solvent, boiling under atmospheric pressure, and the lowering of vapour-pressure is read directly. It is, however, necessary to pay great attention to the manipulation.

DISCUSSION.

Dr. BARGER pointed out that, although the freezing point and the boiling point methods might be considered preferable for ordinary purposes, the value of vapour-pressure methods lay in the possibility of applying them to special cases where other methods failed. This was found to be the case with the microscopical vapour-pressure method described by him a year ago.

Mr. BALY pointed out that in all probability the determination of molecular weights by the vapour-pressure of a solution would be vitiated owing to a difference in the concentration in the surface layer, more than would be the case in observing the boiling point of the solution. In the latter method, a very rapid renewal of surface was taking place, whilst in the former, one is dependent more or less upon a constant surface. He asked whether the author had taken care to shake his apparatus, since differences of concentration in the surface are known to occur, as, for example, in solutions of butyl alcohol.

Mr. ARTHUR MARSHALL said he could corroborate the statements made as to the practicability of ascertaining molecular weights by means of vapour-pressure measurements. He described a simple apparatus he had used in determining the vapour tension of binary liquids, in which the difficulty of obtaining a liquid in a uniform condition was overcome by employing a small glass rod placed in such a manner that when the apparatus was shaken the rod stirred the liquid. But even with this precaution he had found that in order to obtain a state of equilibrium it was necessary to allow the apparatus to remain at constant temperature for several hours with occasional shaking.

15. "Note on β-NH-ethenyl-diaminonaphthalene." By RAPHAEL MELOOLA and JOSEPH HENRY LANE.

The ethenyl-diaminonaphthalene, obtained by Prager in 1885 by debrominating the bromoanhydro-base prepared by the reduction of 4-bromo-2-nitroaceto-α-naphthalide (*Ber.*, 1885, xviii., 2161), has been assumed in our former paper (*Trans.*, 1904, lxxv., 1594, footnote) to be identical with the anhydro-base obtained from Markfeldt's ethenyltriaminonaphthalene by the diazo-method. We have already pointed out (*loc. cit.*) that no direct proof of this identity has hitherto been given, and we have accordingly repeated Prager's experiments with certain modifications, which throw further light on the general nature of the isomerism which has formed the subject of our investigations. The bromonitroaceto-α-naphthalide was reduced with iron and hydrochloric acid instead of with stannous chloride, as in Prager's method, and the bromoanhydro-base was found to be identical with that obtained by the author named. This result is of importance as supporting the hypothesis that the isomerism of the ethenyltriaminonaphthalenes is due to the simultaneous or successive reduction of the nitro-group (*loc. cit.*, p. 1595). When the 4-position is occupied by a bromine atom instead of by a nitro-group, the nature of the reducing agent makes no difference in the nature of the bromoamide. Iron and tin both give the same product. The latter was debrominated by boiling for two days in alcoholic solution with zinc dust and alkali, and the amidine thus obtained was found to be identical in every respect (m. p. of picrate, &c.) with Prager's base. The latter is therefore now conclusively shown to be the β-NH-amidine, as formerly assumed, the transference of the NH-group from the α- to the β-position taking place simultaneously with the removal of the bromine atom in the manner indicated in our last paper (*loc. cit.*, p. 1594).

PHYSICAL SOCIETY.

Annual General Meeting, February 10th, 1905.

Dr. R. T. GLAZEBROOK, F.R.S., President, in the Chair.

THE Report of the Council was read by the Secretary.

Since the last Annual General Meeting thirteen Science Meetings of the Society have been held. Of these, eleven were held at the Royal College of Science; one, that on November 25th, was held at the Finsbury Technical College, and one, on December 9th, at the Central Technical College, South Kensington. The average attendance at the meetings has been 43, the number being somewhat larger at the evening than at the afternoon meetings. Additional interest has been given to the meetings by the increase in the number of experiments shown to illustrate the papers.

The number of Fellows now on the roll is 425, an increase of 7 over the number last year. Fourteen new Fellows have been elected. There have been four resignations, and the Society has to mourn the loss by death of one Honorary Fellow, Prof. Villari, and three Fellows, namely, Prof. J. D. Everett, W. T. Goolden, and Dr. Lawson.

The Council have co-operated with the Institution of Electrical Engineers in bringing *Science Abstracts* up to date. This has entailed a rather heavy expenditure, which, however, the Council felt was fully justified by the importance of the work. The Council are glad to be able to report that the publication has now been brought up to date, and in future the Society will be liable only for the usual annual contribution. The agreement with the Institution referred to in the last report has not yet been executed, owing to difficulties in making an agreement exactly on the lines which were proposed. Some alterations in detail have therefore been made, and a three years' agreement will shortly be executed, dating from the beginning of the present year.

During the year the President signed on behalf of the Council a petition in support of a Bill for the Metric System.

The Report of the Treasurer for the year 1904 was read by the Secretary.

Additional expenditure was incurred last year amounting to £115 in bringing *Science Abstracts* up to date, which has the effect of reducing the balance in the bank as compared with that at the beginning of the year. But the income from subscriptions has increased, so that the reduction of the balance is less than the extraordinary expenditure. The value of some of the securities has declined, but others have risen, so that on the whole the position of the Society remains almost unchanged.

The following Officers and Council were elected for the ensuing year:—

President—Prof. J. H. Poynting, D.Sc., F.R.S.

Vice-Presidents—Those who have filled the Office of President together with C. Chree, D.Sc., F.R.S.; H. M. Elder, M.A.; Prof. J. A. Fleming, M.A., D.Sc., F.R.S.; J. Swinburne.

Secretaries—W. Watson, D.Sc., F.R.S., and W. R. Cooper, M.A.

Foreign Secretary—Prof. S. P. Thompson, D.Sc., F.R.S.

Treasurer—Prof. H. L. Callendar, M.A., F.R.S.

Librarian—W. Watson, D.Sc., F.R.S.

Other Members of Council—T. H. Blakesley, M.A.; C. V. Boys, F.R.S.; A. Campbell, B.A.; Prof. W. Cassie, M.A.; W. B. Croft, M.A.; W. Duddell; W. A. Price, M.A.; S. Skinner, M.A.; Prof. F. T. Trouton, Sc.D., F.R.S.; Prof. S. A. F. White, M.A.

Prof. POYNTING then took the Chair, and delivered an address on "Radiation Pressure."

A hundred years ago, when the corpuscular theory held almost universal sway, it would have been easier to explain the pressure of light than it is to-day, when it is certain

that light is a form of wave-motion. The means at the disposal of early experimenters were inadequate to detect so small a quantity; but if the eighteenth century philosophers had been able to carry out the experiments of Lebedew and of Nichols and Hull, and had they further known of the emission of corpuscles revealed to us by the kathode stream and by radio-active bodies, there can be little doubt that Young and Fresnel would have had much greater difficulty in dethroning the corpuscular theory, and setting up the wave theory in its place. The existence of pressure due to waves, though held by Euler, seems to have dropped out of sight until Maxwell, in 1872, predicted its existence as a consequence of his electromagnetic theory of light. The first suggestion that it is a general property of waves is probably due to Mr. S. T. Preston, who in 1876 pointed out the analogy of the energy carrying power of a beam of light with the mechanical carriage by belting, and calculated the pressure exerted on the surface of the sun by the issuing radiation. It seems possible that in all cases of energy transfer, momentum, in the direction of transfer, is also passed on, and that there is, therefore, a back pressure on the source. Though there is as yet no general and direct dynamical theorem accounting for radiation pressure, Professor Larmor has given a simple indirect mode of proving the existence of the pressure which applies to all waves in which the average energy density for a given amplitude is inversely as the square of the wave-length. He has shown that when a train of waves is incident normally on a perfectly reflecting surface, the pressure on the surface is equal to $E(1 + 2u/U)$, where $E/2$ is the energy density just outside the reflector in the incident train, U is the wave-velocity, and u the velocity of the reflector supposed small in comparison with U . In a similar manner it can be shown that there is a pressure on the source, increased when the source is moving forward, decreased when it is receding. It is essential, however, that we should be able to move the reflecting surface without disturbing the medium except by reflecting the waves. Though Larmor's proof is quite convincing, it is interesting to realise the way in which the pressure is produced in the different types of wave-motion. In the case of electro-magnetic waves, Maxwell's original mode of treatment is the simplest. A train of waves is regarded as a system of electric and magnetic tubes transverse to the direction of propagation, each kind pressing out sideways; that is, in the direction of propagation. They press against the source from which they issue, against each other as they travel, and against any surface on which they fall. In sound-waves there is a node at the reflecting surface. If the variation of pressure from the undisturbed value were exactly proportional to the displacement of a parallel layer near the surface, and if the displacement were exactly harmonic, then the average pressure would be equal to the normal undisturbed value. But consider a layer of air quite close to the surface. If it moves up a distance, y , towards the surface, the pressure is increased. If it moves an equal distance, y , away from the surface, the pressure is decreased, but to a slightly smaller extent. The excess of pressure during the compression half is greater than its defect during the extension half, and the net result is an average excess of pressure on the reflecting surface. Lord Rayleigh, using Boyle's law, has shown that this average excess should be equal to the average density of the energy just outside the reflecting surface. In the case of transverse waves in an elastic solid, it can be shown that there is a small pressure perpendicular to the planes of shear; that is, in the direction of propagation, and that this small pressure is just equal to the energy density of the waves. The experimental verification of the pressure of elastic solid waves has not yet been accomplished, but the pressure due to sound-waves has been demonstrated by Altberg, working in Lebedew's laboratory at Moscow, the pressure obtained sometimes rising to as much as 0.24 dynes per sq. c.m. By means of a telephone manometer it was found, that through a large range the pressure exerted on a surface was proportional to the intensity of the sound.

Both theory and experiment justify the conclusion that when a source is pouring out waves, it is pouring out with them forward momentum which is manifested in the back pressure against the source, and in the forward pressure when the waves reach an opposing surface, and which, in the meanwhile, must be regarded as travelling with the train. It was shown that this idea of momentum in a wave-train enables us to see the nature of the action of a beam of light on a surface where it is reflected, absorbed, or refracted without any further appeal to the theory of the wave-motion of which we suppose the light to consist. In the case of total reflection there is a normal force upon the surface, in the case of total absorption there is a force normal to the surface, and a tangential force parallel to the surface; while in the case of total refraction there is a normal force which may be regarded as a pull upon the surface or a pressure from within. In any real refraction there will be reflection as well, but with unpolarised light, in the case of glass, a calculation shows that the refraction-pull is always greater than the reflection-push, even at grazing incidence. An experiment, made by the President in conjunction with Dr. Barlow, was described to serve as an illustration of the idea of a beam of light being regarded as a stream of momentum. A rectangular block of glass was suspended by a quartz fibre so that the long axis of the block was horizontal. It was hung in an exhausted case with glass windows, and a horizontal beam of light was directed on to one end of the block so that it entered centrally, and emerged centrally from the other end after two internal reflections. Thus a stream of momentum was shifted parallel to itself, or in this particular case a counter-clockwise couple acted on the beam. By suitable means the clockwise couple on the block, due to the pressures at the two internal reflections, was distinctly observed and approximately measured. The result obtained was of the same order as that deduced from the measurement of the energy of the beam by means of a blackened silver disc.

The extreme minuteness of these light forces appears to put them beyond consideration in terrestrial affairs, but in the Solar system, where they have freer play, and vast times to work in, their effects may mount up into importance. On the larger bodies the force of the light of the sun is small compared with the gravitational attraction, but as the ratio of the radiation pressure to the gravitation pull varies inversely as the radius if the density is constant, the pressure will balance the pull on a spherical absorbing particle of the density of the earth if its diameter is about a hundred-thousandth of an inch. The possible effects of radiation-pressure may be illustrated without going to such fineness as this. In the case of a particle of the density of the earth, and a thousandth of an inch in diameter, going round the sun at the earth's distance, there are two effects due to the sun's radiation. In the first place, the radiation-push is $\frac{1}{10}$ of the gravitation-pull, and the result is equivalent to a diminution in the sun's mass. In the second place, the radiation absorbed by the particle and given out again on all sides, is crushed up in front as the particle moves forward, and is opened out behind. There is thus a slightly greater pressure on the advancing hemisphere than on the receding one, and this appears as a small resisting force in the direction of motion. Through this the particle tends to move in a decreasing orbit, spiralling in towards the sun. As there is good reason to believe that some comets, at least, are composed of clouds of dust, there is hope that some of their eccentricities may be explained by the existence of radiation pressure. If the particles of a dust cloud circling round the sun are of different sizes or densities, the radiation accelerations on them will differ. The larger particles will be less affected than the smaller, will travel faster round a given orbit, and will draw more slowly in towards the sun. Thus a comet of particles of mixed sizes will gradually be degraded into a diffused trail lengthening and broadening, the finer dust on the inner and the coarser on the outer edge. If a planet, while still radiating much energy on its own account captures and attaches to itself, as a satellite, a cometary

cloud of dust in which there are several different grades, with gaps in the scale of size, it may be possible that in course of time the radiation-pressure effects will form the different grades into different rings surrounding the planet. Such may possibly be the origin of the rings of Saturn.

NOTICES OF BOOKS

The Spinning and Twisting of Long Vegetable Fibres. By HERBERT R. CARTER. London: Charles Griffin and Co., Ltd. 1904.

THIS book covers a very extensive ground, dealing as it does with methods now generally employed for hacking, carding, preparing, spinning, and twisting the long vegetable fibres of commerce, and it appears rather doubtful whether such a variety of subjects can be successfully treated in one volume of only moderate size in such a way as to be really useful to the student or practical man. However, those interested in the textile industries will no doubt derive some useful hints and information from the book, which is very evidently the work of one who is thoroughly at home amongst the various mechanical appliances which he describes with considerable attention to detail. The illustrations and sectional drawings are copious, and the latter especially are thoroughly well executed.

The Dynamical Theory of Gases. By J. H. JEANS, M.A. Cambridge: The University Press. 1904.

IN this volume, which represents an important contribution to our knowledge of the theory of gases, an attempt is made to develop the theory upon a strictly mathematical basis. Hence it is of course clear that only those who have had a fairly extensive mathematical training ought to think of trying to cope with the difficulties encountered in reading it. The discrepancies between results as foretold by theory, e.g., in the case of the theorem of equipartition of energy and the evaluation of the ratio of the specific heats of a gas, and the results actually obtained by experiment, are well discussed, and the author successfully keeps before the student the necessity for constantly bearing in mind the exact relation between premises and conclusions. The interpretation of the phenomena discussed and experimental results are briefly considered at intervals throughout the work, and these little oases in the desert of mathematical analysis are refreshing and interesting; as, for instance, in the consideration of the evidence which has been obtained as to the size of molecules.

Application of some General Reactions to Investigations in Organic Chemistry. By Dr. LASSAR-COHN. Authorised Translation of J. BISHOP TINGLE, Ph.D. (Munich), F.C.S. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1904.

IN this small book are described various suggestions for the simplification of some practical problems which come to light during the study of the preparation of organic compounds. It is well known that certain general methods are not attended with success when applied in particular cases, leading frequently to the formation of unexpected products, and the author now attempts to give some explanation of these anomalous results, to elucidate the causes which have led to them, and the means by which they may be avoided. The work is partly of a practical and partly of a theoretical nature, and aims at introducing system into a region at present in a somewhat chaotic state of confusion. Some of the explanations, as, for instance, that of the "protective action" of certain atomic complexes, are hardly explanations at all in the true sense of the word, but simply represent the introduction of a new name for a still obscure phenomenon, but the chief value of the book will

undoubtedly be best realised by research students. No better book could be put into their hands to start them on the right track, and suggest fresh investigations aiming at the elucidation of some definite and important problem, and while it will help them possibly in unexpected difficulties, it will force them to think for themselves and plan out an original line of action. The work has another value, in that it collects and puts in a new light certain isolated syntheses and preparations which have not been previously subjected to examination as a whole, and as compared with the results of various workers, and all interested in organic chemistry will derive both information and stimulus from its perusal.

Manual of Chemical Analysis. By EUGENE PROST, D.Sc. Translated by J. CRUICKSHANK SMITH, B.Sc., F.C.S. London: MacLaren and Sons. New York: D. Van Nostrand Company. 1904.

THIS book contains details of methods of analysis of the most important native and manufactured products, fuels, ores, metals, alloys, and salts, and is intended specially for use by metallurgical chemists. According to the translator it covers an important field not dealt with elsewhere in the same fashion and to the same effect, and though there can be no question that the author has succeeded in compressing a very large quantity of material into a comparatively small space, the process of compression has robbed the information of much of its usefulness from a practical point of view. To take an example, in the case of the determination of copper by electrolysis, which may be regarded as the most convenient and reliable method, the details of current, manipulation, &c., would probably not be found sufficient to enable a determination to be performed without reference to some other authority. Again, in the description of the analysis of chromite, the comparatively simple and rapid method of determining the chromium alone by means of the volumetric process is not mentioned; and the precipitation of cadmium from acid solution as sulphide, though it must be confessed that it is a method which is often recommended, does not give good results owing to the formation of basic salts; at any rate an alternative method should be described in a case like this. Such omissions detract from the value of the book, which, however, certainly possesses decided merits, being exceedingly concise and thoroughly practical in all respects.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxi., No. 3, January 16, 1905.

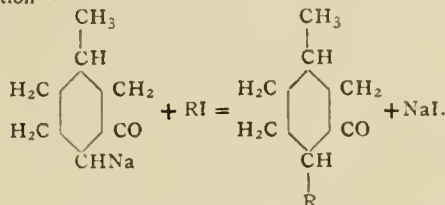
Physical Constants of Calcium and Calcium Amalgam.—H. Moissan and M. Chavanne.—The authors find the electrical conductivity of calcium to be 15.6 at 20° compared with silver 100. The fusing-point is 810°, but at 790° to 795° the calcium passes into a pasty state. The density of calcium they find lying between 1.525 and 1.560. They also investigate the properties of the crystalline calcium amalgam; this is stable in dry air, and absorbs neither nitrogen nor oxygen. In damp air, on the contrary, it is rapidly affected, and becomes transformed into a mixture of lime and finely-divided mercury. It acts chemically as a strong reducing agent.

Synthesis of Menthone and Menthol.—A. Haller and C. Martine.—In order to verify the constitution of menthone and menthol, the authors obtain the homologues and isomers of menthone, starting from menthol.

Compounds of Samarium Chloride with Ammonia Gas.—C. Matignon and R. Trannoy.—Samarium chloride, when freshly prepared and anhydrous, absorbs ammonia

gas in considerable quantity in the cold. The substance formed is identified by the decided increase in volume of the material, which becomes whiter and finally loses the pale yellow colour altogether. The authors investigate the properties of the various compounds which are formed during the reaction, and prove that samarium chloride forms with ammonia gas eight compounds dissociable at definite temperatures.

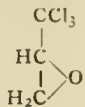
β-Methyl-α-alcylcyclohexanones and their corresponding Alcohols. Homologues of Menthone and Menthol.—A. Haller.—β-Methylcyclohexanone, whether prepared by decomposition of pulegone or by hydrogenation of metacresol, when subjected to an analogous reaction, gives rise to homologues of menthone, according to the equation—



The principal fractions which can be isolated are:—Dimethylcyclohexanone, $\text{C}_8\text{H}_{14}\text{O}$; trimethylcyclohexanone, $\text{C}_9\text{H}_{16}\text{O}$; tetramethylcyclohexanone, $\text{C}_{10}\text{H}_{18}\text{O}$; pentamethylcyclohexanone, $\text{C}_{11}\text{H}_{20}\text{O}$.

An Isomer of Trichlorated Acetone.—G. Perrier and E. Prost.—The authors prepare a new body having the empirical formula of trichlorated acetone, $\text{C}_3\text{Cl}_3\text{H}_3\text{O}$, but having totally different properties. This body is insoluble in water and unacted upon by ammonia either when hot or when cold. All the chlorine seems to be attached to the same atom of carbon, because the action of hot sulphuric acid causes chloral to be formed, and oxidation by means of the chromic mixture gives chloroform.

Finally, the action of hot potash and aniline in alcoholic solution produces carbylamine, recognised by its smell. The accompanying formula can be announced as the probable formula which would make the substance an oxide of trichlorated propene. The authors are continuing their investigation in order to confirm this formula.



Migration of the Ethylenic Liaison in Non-saturated Acyclic Acids.—E. E. Blaise and A. Luttringer.—When α-bromo-ethers corresponding to the formula $\text{R}-\text{CHBr}-\text{CO}-\text{OC}_2\text{H}_5$ are condensed with trioxymethylene in presence of zinc, and the product of the reaction is decomposed by water, α-alcylhydracrylic ethers are obtained, which, when dehydrated, give α-alcylacrylic ethers. The authors observe that sulphuric acid, under favourable conditions, is capable of causing an inverse migration of the ethylenic liaison of the α-alcylacrylic acids.

Union of Natural Leucine with Carbamic Acid.—M. Hugounenq and Albert Morel.—The authors endeavour to unite amido-acids by trying to place them in the same molecule of substituted urea, $\text{CO} \begin{array}{c} \text{NH}-\text{R}-\text{COOH} \\ \text{NH}-\text{R}-\text{COOH} \end{array}$, and find that urea can be made to unite with natural leucine.

A New Method of Synthesis of Saturated Ketones by the Method of Catalytic Reduction.—M. Darzens.—The non-saturated ketones can easily be prepared by the condensation of aldehydes with ordinary acetone, and from this may be deduced a general and practical method for the preparation of saturated ketones by causing a fatty aldehyde in C_n to pass into a saturated ketone in C_{n+3} . The author finally describes a method of synthesis of aldehydes which start from saturated ketones. By uniting these two methods of synthesis, the passage of a fatty aldehyde in C_n into the superior homologue in C_{n+4} can be realised.

MEETINGS FOR THE WEEK.

MONDAY, 20th.—Society of Arts, 8. (Cantor Lecture). "Internal Combustion Engines," by D. Clerk, M.Inst.C.E.
 TUESDAY, 21st.—Royal Institution, 5. "The Structure and Life of Animals," by Prof. L. C. Miall, D.Sc., F.R.S.
 — Society of Arts, 8. "The Queen Victoria Memorial as compared with other Royal Memorials Abroad," by Marion H. Spielmann, F.S.A.
 WEDNESDAY, 22nd.—Society of Arts, 8. "Some Misconceptions of Musical Pitch," by John E. Burlingame.
 THURSDAY, 23rd.—Royal Institution, 5. "Recent Work of the Geological Survey," by Prof. J. J. H. Teall, F.R.S., &c.
 — Society of Arts, 4.30. "The Indian Census of 1901," by Sir Charles A. Elliott, K.C.S.I., &c.
 FRIDAY, 24th.—Royal Institution, 9. "Fungi," by Prof. Marshall Ward, F.R.S., &c.
 — Physical, 5. "The Curvature Method of Teaching Geometrical Optics," by Dr. C. V. Drysdale. Exhibition of Dr. Meissling's Colour Patch Apparatus, by R. J. Sowter. A Method of Illustrating the Laws of the Simple Pendulum, and an Exhibition of String Models of Optical Systems, by J. Schofield.
 SATURDAY, 25th.—Royal Institution, 3. "Archæology," by David G. Hogarth, M.A.

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THE CHEMICAL NEWS.

VOL. XCI., No. 2361.

NEW EXPERIMENTS ON THE PREPARATION OF DIAMONDS.

By HENRI MOISSAN.

As a sequel to my researches on the meteorite found in Cañon Diablo, I have further developed certain experiments regarding the reproduction of the diamond.

I repeated the experiments which were described in a previous paper ("Researches on Different Varieties of Carbon," *Ann. de Chem. et de Phys.*, viii., pp., 289, 306, 466), and obtained the same results; that is, wedge-like crystals with square impressions on them were formed. Also drops and octahedra with curved faces. These crystals were perfectly transparent, and of great refrangibility. They have a density of about 3.5, so that they sink in methylene iodide of density 3.4. They scratch rubies, and burn in oxygen without ash, producing carbon dioxide only.

Some of them split shortly after their preparation; the same thing, however, happens to certain Cape diamonds when they are separated from the blue earth brought up from the deep mines of the Transvaal.

My experiments were repeated by Sir William Crookes (*Proc. Roy. Inst.*, xv., p. 477), who obtained in the same way both black and transparent diamonds. M. Majorana applied an external pressure to the fused iron saturated with carbon, and thus prepared microscopic transparent diamonds.

However, my experiments on the block of iron, 183 k.grms., from Cañon Diablo, have shown that diamonds are hidden in the fissures of the meteorite in the same medium of metal. Further, these fissures were found to be connected by narrow openings with the nodules of iron sulphide or troilite, which I described in collaboration with M. Osmond in a preceding paper.

It therefore appears logical to admit that the sulphur assists the displacement of the carbon in the iron carbide.

Besides the troilite I also showed that the Cañon Diablo meteorite contained silicon in the form of carbon silicide, and also phosphorus. These different non-metals have probably helped towards the separation and the crystallisation of the carbon.

I continued the study of this question, and operated in the following manner:—150 grms. of Sweden iron, broken into fragments of a few c.c. volume each, are melted in the electric furnace in presence of sugar carbon. The saturation of the iron with carbon at the temperature of the electric furnace is completed in two or three minutes with a current of 400 amperes under 120 volts pressure. The crucible containing the liquid iron is removed from the furnace, and a solid fragment of iron mono-sulphide of about 5 grms. is added. This melts also, and mixes with the mass. The metal swells, and gases are evolved in abundance. After cooling, the metallic mass is treated with acids. The graphite is transformed into graphitic oxide, then into pyrographitic oxide, and this latter compound is destroyed by a mixture of boiling sulphuric acid, into which, a small quantity at a time, is thrown about 5 grms. of potassium nitrate. After alternate treatments of this residue with hydrofluoric and sulphuric acids and then fusion with the fluohydrate of potassium fluoride, it is decanted, dried, and treated with methylene iodide of density 3.4. The portion falling to the bottom is collected. Under these conditions I never found any diamonds.

The results are quite otherwise if the crucible containing the liquid iron is rapidly cooled, and added to the iron sulphide in a quantity of cold water.

The porous graphite vessel is rapidly penetrated by the water, the metallic mass is cooled externally, forming a solid crust, and under these conditions it is evident that an internal pressure is produced, and the carbon which is deposited from the still liquid central part takes the form of diamonds. The appearance of the metallic ingots to which the sulphur is added is naturally rather different from the iron ingots ordinarily cooled in water. There is a similar external resisting portion, but the upper surface of the metal, if the melt and the iron sulphide are rapidly cooled, is covered with a black solid spongy-looking mass, proving the rapid solidification of the emulsionised metal during a brisk gaseous evolution. If the gas had time to be evolved before immersion in water the ingot presents a normal appearance. The diamonds which I obtained by this addition of iron sulphide are of the same form as those formerly prepared. They have the appearance of drops with octahedral ends, composed of superposed layers with curved faces. I obtained several of these octahedra, the different crystals being mounted in Canada balsam, and placed between two glass plates. I presented some of these specimens to the Académie.

Certain of these crystals broke a few weeks after their preparation, others contained flaws, and a large number have surface blemishes, either square or parallel striae, in the same way as natural diamonds. All have a rather greasy aspect and a high refractive index. I heated a few in oxygen in a tiny platinum boat which I described in my former paper on diamond manufacture. They burn, leaving no ash. The only difference which the addition of iron sulphide seems to make is that the yield, always, however, very small, is distinctly higher than any previously obtained. In a single ingot I have collected eight to ten little diamonds, of which half or two-thirds could be separated with a steel needle without a magnifying glass.

I performed several series of experiments by adding either iron silicide or melted silicon to the iron previously saturated with carbon at the temperature of the electric furnace before the rapid cooling in water.

In this case diamonds were also obtained. and I think the yield was greater than that in the previous experiments I described. However, the large quantity of carbon silicide produced, above all when melted silicon is employed, renders the separation by means of methylene iodide much more difficult.

It must not be forgotten that the carbon silicide prepared in the iron is always blue or green, as was shown in 1893, and so it is impossible, if we examine the silicide under the microscope, to confuse these with the black or transparent diamond fragments. Besides, the density being only 3.12 they float on the surface of methylene iodide.

Diamonds prepared with silicon have a more irregular form than those prepared by the former method. There are also a larger proportion of flawed and black diamonds. Under these conditions also I obtained a large number of diamonds having square surface impressions. The extremities of some were terminated by chapelets of pillared cubes. Some of the diamonds which were cracked for some weeks and even some months after their preparation, showed the fissures covered with minute cubes. By this preparation the drop form is rarer and there are no octahedra. The yield is also a little higher than that obtained in my experiment of 1893. In several cases I separated 10 to 15 microscopic diamonds from a single ingot. The larger of these are about 0.75 m.m. long, the octahedra being 0.2 m.m., and many of the drops being 0.4 to 0.1 m.m. long.

These diamonds are of the same order of greatness as those which were extracted from the Cañon Diablo meteorite of 183 k.grms., some of them being even a little larger. They are all, however, practically microscopic particles.

Two series of experiments made under the same conditions with iron phosphide gave no diamonds.

Optical Properties.—Synthesised diamonds have a characteristic greasy aspect and a high refractive index. This latter property can be used after a little practice as a

means of distinguishing the diamonds from other transparent substances with which they may be mixed.

I also examined the action of these synthesised diamonds on parallel and convergent polarised light. I found that their double refrangibility, always very small, is of variable magnitude and has no relation to the external form. In particular, with convergent light, the very fine and the very strong neutral lines are the only ones noticed, and I was able to draw certain conclusions from their appearance.

Finally, we conclude that the optical characteristics of these crystals in polarised light are not constant. The crystals are very slightly doubly refracting. As a result of my experiments on the relationship between these and a known crystal under similar conditions I found that there is no relationship between these diamonds and such crystals as carbon silicide. The latter present a normal double refrangibility much higher than the diamonds. Also, the carbon silicide prepared from iron is always strongly coloured, the carbon silicide from Cañon Diablo being green.

Further, this action of crystallised carbon on polarised light has been known for some time. Besides belonging to the cubic system the ordinary diamond presents very noticeable phenomena of double refraction. This was investigated first by Brewster (*Phil. Trans.*, cv., p. 31; cvi., p. 167; cviii., p. 255; and *Edinburgh Trans.*, xxiii., p. 41), and since noticed by Jannettaz, Hirschwald, Mallard, and Reinhard Brauns. Des Cloizeaux noticed that a large number of crystals show irregular colours in polarised light. According to Hirschwald the phenomenon is almost general. Jannettaz admits that the double refracting power of the diamond proves the existence of internal pressure or the phenomena of strain. Brauns explains that the double refraction of the diamond is due to internal strain, and thus the fact of the mineral being formed under the action of strong pressure is proved. Cohen examined a diamond presenting the phenomena of polarisation in which the colours were as vivid as in a crystal of quartz.

To-day we know that the majority of cubic crystals frequently show phenomena analogous to double refraction, such as alum, analcime, lead nitrate, blende, &c.

At the conclusion of these different series of experiments I did not re-investigate the combustion by weight of synthesised diamonds, because I thought that the three analyses published in 1894 were sufficient to settle the question. Referring to these I find that, in the first, 6 m.grms. of black diamonds gave 23 m.grms. of carbon dioxide, and that the ash remaining after the combustion was imponderable. In the second experiment 15 m.grms. of transparent fragments were burnt, and left a residue of 2.5 m.grms. of brilliant rounded grains which would not burn in oxygen at 1000° C. These grains were not ashes from the diamond. They were formed of a transparent substance rich in silicon, which disappeared after fusion with a fluohydrate of potassium fluoride. The weight of 13 m.grms. of the transparent diamonds burnt during this analysis gave 49.6 m.grms. of carbon dioxide.

Finally, in the third combustion, 5.7 m.grms. of transparent diamonds, treated this time before combustion with fluohydrate of potassium fluoride, yielded 20.5 m.grms. of carbon dioxide. The ashes again did not affect the balance.

These three experiments are sufficient to establish the fact that the microscopic fragments obtained during my researches are formed of pure carbon.

The new experiments which I have here published as a continuation of my investigations of the Cañon Diablo meteorite merely corroborate my previous researches. I have always regarded the diamond as that variety of carbon which had been liquefied under a great pressure, whilst I proved a long time ago that at ordinary pressure all specimens of carbon under the action of a very high temperature vaporise without passing into the liquid state, and always yield the same variety of carbon—namely, graphite.—*Comptes Rendus*, cxl., No. 5, p. 277.

THE OCCURRENCE OF RADIUM AND RADIO-ACTIVE RARE EARTHS IN FANGO MUD AND IN EARTH FROM THE FIELDS OF CAPRI.

By F. GIESEL.

THE work of Elster and Geitel has shown that radio-active substances (radium) occur widely distributed in different kinds of earths, especially in sediments from thermal springs and in volcanic earths.

The activity of Fango and Capri earth is certainly very small compared with that of pitchblende (only about one-thousandth part); nevertheless, the method of separating radio-active substances usually adopted in the case of the uranium ores has the desired result, owing to the insolubility of radium-barium sulphate and its property of bringing down with it the radio-active rare earths.

For the investigation we used—(1) Fango mud with about 30 volts leakage, and (2) ordinary earth from the fields of Capri (which Dr. Cuomo, of Capri, kindly sent us), having about the same activity.

1. From 60 kilograms. of moist mud a small quantity of raw barium sulphate was obtained, which yielded 0.39 gm. of barium carbonate and 0.05 gm. of ammonia precipitate. But the extraction was by no means exhaustive. Both preparations excite the barium-platinum cyanide screen, especially the barium salt. As both of them have retained their maximum activity for half a year after reaching it, there can be no doubt that they contain, on the one hand, radium, and on the other, emanium (determined by the decay curve and the behaviour of the Sidot's blende screen towards the emanation).

2. From 40 kilograms. of the earth from the fields of Capri the barium present (as well as a large amount of calcium) could be extracted directly by means of hydrochloric acid, as, strangely enough, no trace of sulphuric acid was present. The first extraction, which was performed without excess of hydrochloric acid, gave, on addition of sulphuric acid, a raw barium sulphate precipitate which yielded:—

- I. 8.9 grms. of barium carbonate with an original activity of 4078 volts,* and after about three weeks 1222 volts leakage.
- 0.25 gm. of oxalate of rare earths of the cerium group (strong didymium lines), with original activity 94,000 volts, after about three weeks 95,000 volts leakage.
- 1.3 grms. of ammonia precipitate, which still contained traces of radium, with original activity 159,000 volts, and after about three weeks 194,000 volts leakage.

On again extracting with a small excess of hydrochloric acid we obtained:—

- II. 2.82 grms. of barium carbonate with an original activity of 13,276 volts, and after about three weeks 16,820 volts leakage.

And on extracting a third time with a larger excess of acid we obtained:—

- III. 0.15 gm. of barium carbonate with 33,000 volts and after about three weeks 192,000 volts leakage

Thus it appears that most of the activity of barium carbonate I. was only induced. Carbonate II. contains more radium, while the most is present in carbonate III. of the last extraction. Barium carbonates I. and II. were converted into bromide and submitted to fractional crystallisation. The most difficultly soluble fraction (about $\frac{1}{2}$ gm.) on removal of the water showed distinct self luminescence.

Uranium could not be found in the two earths examined—*Berichte*, 1905, xxxviii., 132.

* The voltage numbers refer to a leakage in Elster and Geitel apparatus for 125 grms. of the substance in an hour.

THE USE OF CALCIUM IN LECTURE-TABLE EXPERIMENTS.

By ALFRED SENIER, Ph.D.,
Professor of Chemistry, Queen's College, Galway,
and

ROSALIND CLARKE, B.A.,
Demonstrator of Chemistry, Queen's College, Galway.

SCIENCE is indebted to a recent development of German industry for a source of calcium from which this metal may now be obtained in quantities of a pound or more, and at a comparatively trifling cost. It is produced by electrolysis in the form of rough cylindrical sticks weighing about a pound each. In colour it is white, like aluminium, and it has about the same degree of hardness as ordinary brass. It is easily turned in a lathe, and the turnings, which may be allowed to fall into light petroleum, are a convenient form in which to employ it.

Calcium was discovered in 1808 by Davy, but was chiefly studied by Matthiessen and later by Frei. The following suggested applications of the metal to lecture-table experiments depend on reactions described by Matthiessen (*Quart. Journ. Chem. Soc.*, 1856, viii., 29). It is curious that Matthiessen's calcium had a yellow colour, whereas that now in the market is white, in agreement with Davy's observations and those of Frei. From an experiment we made, the commercial metal contains 98 per cent of calcium.

Preparation of Hydrogen from Water.—When wrapped in iron gauze and introduced into a pneumatic trough containing water, in the usual way, hydrogen is evolved quietly, and may be collected readily in any desired quantity. At the same time the water of the trough becomes turbid owing to floating particles of calcium hydroxide. The reaction is so much more moderate and more easily controlled than that with sodium and water, that we venture to suggest that in schools, and generally in the hands of beginners, it be substituted for the latter. Moreover, it is an additional advantage that both products of the reaction, the gas and the solid hydroxide, are observed at once.

Synthesis of Calcium Compounds: Oxide, Chloride, Sulphide, Phosphide.—Calcium turnings were placed in the bulb of hard-glass tube, with a central bulb, in the case of the oxide and chloride experiments. In those of the sulphide and phosphide, tubes with two bulbs were employed, and the second bulb was charged with sulphur and phosphorus respectively, and the end next to it was closed with a cork. In every case the metal was first heated to low redness, and then the dried gas was led over it, or the solid was distilled over it. The oxide, sulphide, and chloride formed at once with brilliant incandescence, but the phosphide was obtained only in small proportions. We examined the light emitted in the oxide and sulphide synthesis, and found that it affected a photographic plate to about the same extent as the burning of the same quantity of magnesium.

Other Attempted Applications.—The reduction of ethyl iodide, in solution in 90 per cent alcohol, was not effected by calcium alone, but ethane was formed when couples of the metal, mixed with either platinum-black or reduced copper, were employed. The ethane, however, appeared to be mixed with hydrogen.

Calcium, burning in air, and then plunged into carbon dioxide, like magnesium, removes the oxygen and liberates carbon. Calcium heated to redness appears to have no action on dried ammonia gas.

STUDIES ON ENZYME ACTION.*

V. HYDROLYSIS OF ISOMERIC GLUCOSIDES AND GALACTOSIDES BY ACIDS AND ENZYMES.

By EDWARD FRANKLAND ARMSTRONG, Ph.D.,
Salters' Company's Research Fellow, Chemical Department, City and Guilds of London Institute, Central Technical College.

IN view of the use constantly made, in contrasting the action of sacroclastic enzymes, of the stereoisomeric α - and β -methyl glucosides and the corresponding galactosides as test materials, it was desirable to gain some idea of the relative stability of these four compounds in presence of acids, and wherever possible towards enzymes, a knowledge of their behaviour being of importance, both as throwing light on their intrinsic properties and for the purpose of correlating the activities of the various compounds amenable to hydrolysis.

As already pointed out (*Proc. Roy. Soc.*, 1904, vol. lxxiii., p. 515), in studying the hydrolysis of sugars under the influence of enzymes, it is difficult to institute just comparisons, as not only, as a rule, is a different enzyme required for each sugar, but we have no means at present of determining the amount of enzyme used; and, sooner or later, it will be necessary to accumulate data correlating one or more analytical factors (nitrogen percentage, &c.) with hydrolytic activity. The difficulty spoken of is enhanced by the fact that, usually, several enzymes occur together—so that no ordinary analytical process can suffice for the determination of the amount of a particular enzyme present in a solution.

On the other hand, it will be of importance to determine whether any one enzyme is capable of hydrolysing several different compounds or whether each particular hydrolysis is ascribable to some one particular enzyme. There is only one case at present known which can be discussed with any degree of certainty. It has been urged by some French workers, especially by Bourquelot and Herissey (*Comptes Rendus*, 1903, vol. cxxxvii., pp. 56, 59), that the action of emulsin on milk sugar is due to the presence of small quantities of lactase, together with the emulsin proper. The following facts, brought forward in Nos. 2 and 3 of this series of papers, may, however, be urged against this view.

(1) The curve expressing the rate at which milk sugar changes is not of the form to be expected if only a very small quantity of enzyme (lactase) were present: in that case a linear expression should apply during the early stages; actually the curve is only of this form when small quantities of emulsin are used.

(2) The action of emulsin on milk sugar is most retarded by glucose, and only to a slight extent by galactose, whereas galactose alone affects the action of lactase. This again would appear to afford proof that the emulsin is directly active.

(3) The curves for emulsin fall off very much more rapidly than those for lactase, showing that the action of the products in removing the enzyme is greater in the former case.

It therefore appears that the differences apparent in the behaviour of emulsin and lactase towards milk sugar are such as to render it improbable that the action of the emulsin is due to the presence of a small proportion of lactase; it would seem, rather, that emulsin is capable of acting on β -galactosides as well as on β -glucosides.†

A different enzyme being required, as a rule, for each sugar, the relative activities of enzymes cannot well be reported in terms of any particular sugar taken as standard; the only method open to us at present is to determine the activity of a particular acid towards the various sugars, and

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* A Paper communicated to the Royal Society, August 26, 1904.

† Pottévin's (*Ann. Inst. Pasteur*, 1903, vol. xviii., p. 31) investigations seem to show, however, that *Aspergillus niger* contains an enzyme which is capable of hydrolysing β -glucosides, but not β -galactosides or milk sugar. It remains an open question whether this "emulsin" is identical with that obtained from almonds.

to estimate, by direct comparison, the activity of the enzyme in terms of this standard acid. But, unfortunately, acids compare very unfavourably with enzymes as hydrolysts: so that, in order to effect hydrolysis at any reasonable rate, it is necessary, except in the case of cane sugar, to operate at elevated temperatures at which a direct comparison between acid and enzyme is impossible. The experiments here described are to be regarded merely as a first attempt in the direction indicated.

Acid Activity.—The method adopted is substantially that previously described. Solutions of the glucoside containing 3 grms. per 100 c.c. were hydrolysed by means of a half-grm. molecular proportion of hydrogen chloride at 74°. The following tables give the results obtained with the various hexosides. The values of the velocity constant K, expressed in the last column, are calculated on the assumption that the change is mono-molecular.

The mean values of K are collected in Table IX., which also contains Sigmond's value for maltose (*Zeit. Phys. Chem.*, 1898, vol. xxvii., p. 385).

It will be noticed that the various hexosides vary widely in stability; the β -glucosides undergoing hydrolysis more rapidly than the stereoisomeric α -compounds—a fact already noted by Alberda von Ekenstein—whilst the galactosides are more rapidly attacked than the corresponding glucosides. These conclusions are in harmony with the well-known fact that the α -compound preponderates in the mixtures obtained in preparing the methyl glucosides and galactosides (*E. Fischer, Ber.*, vol. xxvi., p. 2400; Jungius, *Proc. K. Akad. Wetensch.*, Amsterdam, 1903).

α -Methyl Glucoside.

TABLE I.—Temperature, 74°1'.

Time in hours.	Change in rotation = x.	$K = \frac{1}{t} \log \frac{a}{a-x}$
	Mins.	
2	15	0.00955
4	30	0.00975
7	52	0.01000
17.5	117	0.01010
21	137	0.01027
24	146	0.00977
29	176	0.01047
Total change	a = 350	Mean, K = 0.01

TABLE II.—Temperature, 74°8'.

Time in hours.	x.	K.
	Mins.	
2	18	0.0115
4	34	0.0111
6	48	0.0107
24	174	0.0124
	a = 350	K = 0.0114

β -Methyl Glucoside.

TABLE III.—Temperature, 74°1'.

Time.	x.	K.
	Mins.	
1	11	0.0177
2	22	0.0181
4	41	0.0178
6	60	0.0178
7	69	0.0179
	a = 275	K = 0.0179

TABLE IV.—Temperature, 74°8'.

Time.	x.	K.
	Mins.	
2	28	0.0233
4	50	0.0218
6	70	0.0213
24	193	0.0219
48	253	0.0228
	a = 275	K = 0.0220

α -Methyl Galactoside.

TABLE V.—Temperature, 74°1'.

Time.	x.	K.
	Mins.	
2	72	0.0537
4	125	0.0518
5	150	0.0528
7	196	0.0562
10	240	0.0567
	a = 329	K = 0.0542

β -Methyl Galactoside.

TABLE VI.—Temperature, 74°8'.

Time.	x.	K.
	Mins.	
2	42	0.1066
4	85	0.1059
5.1	105	0.1041
7	121	0.1077
	a = 154	K = 0.1061

Salicin.

TABLE VII.—Temperature, 74°1'.

t.	x.	K.
	Mins.	
1	48	0.0612
2	85	0.0576
3	124	0.0601
4	161	0.0632
6	205	0.0597
8	244	0.0600
	a = 365	Mean, 0.0603

TABLE VIII.—Temperature, 74°1'.

t.	x.	K.
	Mins.	
0.5	26	0.0642
1.5	65	0.0535
2.5	105	0.0589
3.5	141	0.0606
5.5	199	0.0622
7.5	235	0.0598
	a = 365	Mean, 0.0599

TABLE IX.

Hexoside.	$K = \frac{1}{t} \log \frac{a}{a-x}$
	Temperature, 74°1'. Temperature, 74°8'.
α -Methyl glucoside ..	0.0100 0.0114
β -Methyl glucoside ..	0.0179 0.0220
α -Methyl galactoside ..	0.0542 0.0650*
β -Methyl galactoside ..	0.0884* 0.1061
Salicin ..	0.0601
Maltose ..	0.0740

TABLE X.

Time in hours.	Percentage changed = x.	$K = \frac{1}{t} \log \frac{100}{100-x}$
	Mins.	
1	8.7	0.0395
2	16.6	0.0394
3	24.0	0.0397
4	31.3	0.0407
5	37.0	0.0401

TABLE XI.

Time in hours.	α -Methyl glucoside.		Maltose.	
	x.	K.	x.	K.
	Mins.		Mins.	
1	5.55	0.0248	21.2	0.098
2	10.5	0.0241	36.0	0.0969
3	14.8	0.0232	43.0	0.0814
4	18.5	0.0222	49.4	0.0722
5	22.2	0.0218	53.6	0.0667
6	25.9	0.0217	58.2	0.0631

vol. vi., p. 99), and also serve to explain the circumstance that, in separating methyl galactoside (by E. Fischer's method), it is necessary to avoid the presence of acid far more carefully than in separating methyl glucoside.

In the case of the α - and β -glucosides and galactosides, the stereoisomerism in each pair of compounds is confined to the terminal carbon atom; it is, perhaps, noteworthy that there should be so considerable a difference between compounds so related.

But it is even more surprising that a change in the general configuration at the fourth carbon atom, affecting only the nature of the attachment of the oxygen atoms within the ring, such as occurs when glucose passes into galactose, should have so marked an influence on the activity of the group associated with the terminal carbon atom. Such a result enhances the probability of the conclusion that the active system within which the change takes place (compare Armstrong and Caldwell, *Proc. Roy. Soc.*, vol. lxxiii., p. 526) is formed by the association of acid-water molecules with the oxygen atom in the pentaphane ring; in other words, that this oxygen atom is the attractive centre. The argument here made use of renders it desirable that the behaviour of the isomeric mannoses towards acids should also be studied, in order that it may be possible eventually to define more or less accurately the functions of the different oxygen atoms in the molecule.

Enzyme Activity.—At present, the experiments have been confined to two substances, maltose and α -methyl glucoside, which both undergo hydrolysis under the influence of the enzymes contained in ordinary yeast maltase.

Fifty c.c. of a solution containing 5 grms. of α -methyl glucoside was mixed with 50 c.c. of a maltase extract prepared from dried yeast (*Proc. Roy. Soc.*, vol. lxxiii., p. 504); the mixture was kept at 22°. Samples were withdrawn every hour, and polarimetrically examined. Considerable difficulty was at first experienced in obtaining sufficiently clear solutions for this purpose, owing to the impossibility of removing the suspended proteid matter by mere filtration; it was eventually discovered that the liquids could be clarified by means of sodium acetate. The method at present adopted consists in mixing 5 c.c. of water at 100°, containing 0.5 gm. of sodium acetate, with the 5 c.c. withdrawn, then shaking with charcoal and filtering through a double filter. (See Table X.).

To effect a direct comparison of the activity of maltase towards maltose and α -methyl glucoside, the two substances were hydrolysed by the same yeast extract under precisely similar conditions. The extract used in this case was prepared by digesting 5 grms. of dried yeast with 100 c.c. of water at 22° during one hour. (See Table XI.).

It will be seen that the maltose was hydrolysed very much more quickly than the α -methyl glucoside. In both cases the velocity coefficient K diminishes as action proceeds, but to a far greater extent in the case of maltose. This difference is obviously due to the different influence exercised by the products of change in the two cases. It is to be remembered that two molecules of glucose are produced by the hydrolysis of maltose, but only one from α -methyl glucoside; any retardation, therefore which glucoside can effect should be less obvious in the case of the glucoside.

On comparing the results recorded in Tables X. and XI. with those previously given, representing the action of acid, it is obvious that the enzyme was much more active than the acid. About 40 per cent of the glucoside was changed in five hours at 22° by the enzyme; whereas, when acid was used, even in so large a proportion as three molecules of hydrogen chloride to one of glucoside, the same amount of change was effected in only about twenty hours at 75°. As the enzymes are undoubtedly of high molecular weight, and the proportion of maltase in the yeast extract is certainly small, it would seem to follow that the relative molecular activity of the enzyme is very great compared with that of the acid. But, as pointed out in an earlier paper (Part 4, *loc. cit.*), inasmuch as only a small por-

portion of the acid is actually active, it is probable that the enzyme owes its apparent activity to its greater affinity for the sugar, and that in reality the acid has the greater hydrolytic activity.

On account of the rapid alteration in the values of K , it is difficult to make any exact numerical comparison between maltose and methyl glucoside. The initial value of K , in the case of the glucoside, may be estimated at about 0.025; in view of the results previously obtained (*Proc. Roy. Soc.*, vol. lxxiii., p. 508), which throw considerable light on the behaviour of maltose during the early stages of hydrolysis, the corresponding value for this sugar may be set at 0.12 or even higher. Comparing these initial rates, it would appear that maltose is hydrolysed from five to six times as rapidly as α -methyl glucoside, a result of the same order as that deduced in comparing the action of chlorhydric acid on the two hexosides.

Taking into account both the superior stability of the methyl glucoside and the greater influence exercised by the products of change in the case of maltose, the difference in the behaviour of the two compounds on hydrolysis seems to be satisfactorily accounted for.

RAPID ESTIMATION OF PHOSPHORUS IN HÆMATITE PIG-IRON.

By H. PROCTER SMITH, F.C.S.

THE following method has been used by the author for some time for rapidly and accurately determining the amount of phosphorus in pig-iron.

Nothing new is claimed for any of the processes involved, but the author has never heard of this particular modification being used.

The process consists of dissolving the pig-iron in nitric acid of such a strength that most of the silicon is taken into solution, oxidising the phosphorus to ortho-phosphate and carbon to carbon dioxide by permanganate of potash, re-dissolving the oxide of manganese in hydrochloric acid, and precipitating the phosphorus in the usual way with molybdate of ammonia solution, the solution being kept sufficiently diluted all the time in order to prevent any precipitation of silicic acid.

Solutions Required.

Nitric Acid (Sp. gr. 1.12).—Nitric acid (1.4), 300 c.c.; water, 700 c.c.

Permanganate of Potash.—Permanganate of potash (crystals), 25 grms.; water to make 1000 c.c.

Hydrochloric Acid.—Hydrochloric acid (1.2), 500 c.c.; water to make 1000 c.c.

Ammonium Molybdate Solution.—Solution A: Ammonium molybdate (crystals), 50 grms.; water (hot), 100 c.c.; stir until dissolved, cool, and then add ammonia (0.880), 100 c.c.

Solution B: Nitric acid (1.4), 300 c.c.; water, 320 c.c.

When both solutions are perfectly cold add gradually, with constant stirring, Solution A to solution B. If the above conditions are carried out, there will be no precipitation of molybdic acid, and the solution when cold is ready for use.

Ammonia Solution (Sp. gr. 0.90).—Ammonia (0.880), 500 c.c.; water, about 100 c.c. Test this solution with the hydrometer.

Method.

Weigh out into a large beaker 4 grms. of the pig-iron drillings, and pour on 100 c.c. of the nitric acid, boil until dissolved and fumes driven off; filter through a Munckell's Swedish paper, and wash with minimum of water into a conical Phillips beaker; bring filtrate to the boil, then add 10 c.c. of KMnO_4 solution, boil until pink disappears and all the manganese is precipitated, then add 10 c.c. HCl . Now boil over a medium flame until the manganese pre-

precipitate is just dissolved. Put into a beaker 50 c.c. of the ammonium molybdate, and into a separate vessel measure 15 c.c. of the ammonia solution; pour the ammonia into molybdate solution, and add immediately to the beaker just taken from the flame, and shake well. Allow to settle for from five to fifteen minutes and filter through a tared paper; wash with nitric acid (5 per cent solution) and finally water, dry, and weigh. Weight of precipitate $\times 0.4075$ = percentage of phosphorus.

This method has given results which, when checked by standard methods, agree perfectly, and naturally there is a great saving in time by avoiding the tedious evaporation to dryness usually necessary with pig-irons.

All the measurements and details given above are necessary in order to obtain satisfactory results.

By a little modification the process can be used for testing basic iron or foundry iron with equally good results.

Shotton, Flintshire.

ON THE COMPOSITION OF CERTAIN INVERTEBRATE PIGMENTS.

A CHEMICAL STUDY IN ZOOLOGY.

By Dr. A. B. GRIFFITHS.

Calenterata.—The *Cœlenterata* include some of the most beautiful coloured organisms, and their colours are due to the presence of pigments in the tissues; but unfortunately many of these pigments are very unstable, and consequently an examination of them is a matter of great difficulty.

The chief green pigment is chœtopterin, which is extremely susceptible to the action of acids and alkalis, and Krukenberg noticed that the colour of sea-anemones varied according as they secreted a tryptic ferment (acts in an alkaline fluid) or a peptic one (acts in an acid fluid). These facts appear to prove that the various colours of anemones depend upon the secretions of the surrounding tissues. Chœtopterin, bonellin, and enterochlorophyll are the chief green pigments found in the *Cœlenterata*.

Moseley's polyerythrin (red-brown colour) is present in a few anemones, jelly-fish, and corals. This pigment is soluble in acidulated alcohol, or in dilute acid, forming a pink solution with a green fluorescence. The blue pigment cyanein, present in *Cyanea*, *Aurelia*, *Vellela*, and *Rhizostoma*, is soluble in water, and especially sea-water. Cyanein is converted by strong acids, alcohol, benzol, and chloroform into a reddish brown pigment. This reddish brown derivative of cyanein is probably the same pigment that is present in *Chrysaora* (jelly-fish); in fact, the chemical reactions of the two pigments are practically identical.

I have made a study of the red pigment present in *Actinia mesembryanthemum*, and find that it is soluble in alcohol, ether, and other solvents. The pigment was freed from fatty bodies by treating its ethereal solution with a weak solution of NaOH (N/100), and subsequently separating the two liquids. The ethereal solution was evaporated *in vacuo*. The residue was dissolved in pure ether, and again evaporated *in vacuo*. Analyses of the pigment gave the following results:—

0.3670 grm. of pigment gave 0.7736 grm. CO₂ and 0.1750 grm. H₂O.

0.10395 grm. of pigment gave 7.6 c.c. nitrogen at 18° C. and 763 m.m.

	Found.		Calculated for C ₈ H ₉ NO ₃ .
	I.	II.	
Carbon	57.49	—	57.48
Hydrogen	5.29	—	5.38
Nitrogen	—	8.43	8.38
Oxygen	—	—	28.76

The above figures correspond with the formula C₈H₉NO₃ for this pigment.

Solutions of the pigment are optically active, hence there may be one or more asymmetric carbon atoms in the molecule, and the investigation proves that the lower animals are capable of giving rise to asymmetric products.

The optical rotation of the pigment in ether was -0.61° , and the specific rotatory power of the solution was ascertained by using Landolt's formula ("Das Optische Drehungsvermögen Organischer Substanzen"). A determination of the specific rotation, using a solution containing 0.55 grm. of pigment in 100 c.c. of ether in a 2 decimetre tube, gave as the mean of two readings an angle of -0.61° ; hence the specific gravity rotation (specific gravity of the solution, = 0.79):—

$$[\alpha]_D = \frac{100 \times 0.61}{0.55 \times 2 \times 0.79} = -70.19^\circ \text{ at } 18^\circ \text{ C.}$$

The spectrum of the pigment in ether consists of an absorption band at the red end, a partial band from A to C, a complete absorption band to left of D, and an absorption band from F to H'.

There are many other red pigments in the animal kingdom, among them being tetronerythrin, zoonerythrin, and araroth. The first-named pigment is present in certain sponges. It is also present in the red feathers of the flamingo (*Phaenicopterus antiquorum*), in the cardinal bird (*Cardinalis virginianus*), in the red wattles of the male pheasant; in fact, it is widely distributed in the animal kingdom.

Zoonerythrin is a bright red pigment found in the integument of certain sponges, tunicates, crustaceans, and fishes. Gautier says that it aids cutaneous respiration. It is insoluble in water, soluble in alcohol, ether, turpentine, carbon disulphide, and acetic acid. According to Blanchard, this pigment resembles carotin (the lipochrome of the carrot and tomato). Another red pigment is Krukenberg's araroth which is present in the red feathers of certain parrots. Tetronerythrin, zoonerythrin, araroth, and the pigment described in this paper are entirely distinct chemical substances, each with its own characteristic properties.

In 1895, Dr. C. Platt and the author (*Comptes Rendus*, cxxi., p. 451; *Journ. Am. Chem. Soc.*, xvii., p. 877) isolated and described the violet pigment present in *Pelagia*—one of the *Medusæ*.

Echinodermata.—The colours of these animals are numerous and brilliant; and it appears to be a rule that the darker colours (reds, red-yellows, &c.) are found in starfishes that inhabit greater depths of the ocean, while the lighter colours are present in shallow-water forms.

I have already investigated the chemical composition of the pigments of *Echinus esculentus* (*Comptes Rendus*, cxxxi., p. 421) and *Uraster rubens* (*Bull. Soc. Chim.*, Series 3, xxiii., p. 874, in conjunction with F. W. Warren). A red pigment present in the Ophiuroidea (the brittle-stars) appears to be common in several deep-sea forms. The pigment is soluble in ether, alcohol, chloroform, and benzene. An ethereal solution of the pigment (free from fatty bodies) was evaporated *in vacuo*, and an analysis of the residue gave the following results:—

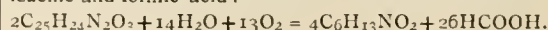
0.2409 grm. of pigment gave 0.65775 grm. CO₂ and 0.13475 grm. H₂O.

0.2709 grm. of pigment gave 17.1 c.c. nitrogen at 16° C. and 759 m.m.

	Found.		Calculated for C ₂₅ H ₂₄ N ₂ O ₃ .
	I.	II.	
Carbon	74.46	—	75.00
Hydrogen	6.20	—	6.00
Nitrogen	—	7.34	7.00
Oxygen	—	—	12.00

The above figures correspond with the formula C₂₅H₂₄N₂O₃ for this pigment.

By boiling with oxidising agents the pigment yielded leucine and formic acid:—



The optical rotation of the pigment in ether was -0.58° , and the specific rotation, using a solution containing 0.38 gm. of pigment in 100 c.c. of ether in a 2 decimetre tube, gave as the mean of two readings an angle of -0.58° ; hence the specific rotation (specific gravity of the solution, $= 0.78$) :—

$$[\alpha]_D = \frac{100 \times 0.58}{0.38 \times 2 \times 0.78} = -97.84^\circ \text{ at } 17^\circ \text{ C.}$$

The spectrum of the pigment in ether consists of an absorption band at the red end, a band from B to C, a band from D to E, and complete absorption from F to H'.

Ophiopholis bellis, which inhabits the seas of North Europe, is brilliantly coloured, and different specimens of the same species exhibit a surprising amount of variation both in their colour and markings. From a chemical standpoint these variations in colour do not appear to be due to different pigments. They are probably isomers, as they all give rise to leucine and formic acid on boiling with oxidising agents.

SOME EXPERIMENTS ON COPPER PIPES.

By SERGIUS KERN, M.E., St. Petersburg.

LATELY we had an opportunity of making some experiments on the nature of cracks and flaws in several steam-conducting red copper pipes of a marine engine, from a vessel provided with Belleville high-pressure boilers.

Four pipes were examined, and samples for chemical analyses and micro-photographs were cut out, quite near the cracks, which were located not far from the flanges. It was ascertained that in flanging the tubes there was in no case overheating of the metal. A sample was taken (No. 5) from a part of a pipe not exposed to the fire, during the flanging operations. The works from which the tubes were received stated that for the production of them the same brand of copper ingots was used.

Chemical analyses showed the following composition of the metal of the four pipes (Nos. 1, 2, 3, 4) and of the sample No. 5 :—

Chemical Analyses of Copper Pipes.

Elements.	Per cent	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Copper ..	..	99.85	99.78	99.86	99.83	99.86
Lead ..	..	0.01	0.009	0.012	0.012	—
Iron ..	..	0.05	0.025	0.04	0.030	—
Bismuth ..	..	0.005	0.003	0.005	0.005	—
Arsenic ..	..	0.02	0.015	0.016	0.010	—
Antimony ..	..	0.003	0.002	0.004	trace	—
Sulphur ..	..	trace	trace	0.002	trace	—
Oxygen (free)	..	0.08	—	0.07	—	—

Sample No. 5 was carefully annealed.

On studying these analyses, only one conclusion can be drawn, that the copper was of very good quality.

The micro-photographs showed the unevenness of the grain; after etching, by dilute nitric acid, the polished surfaces assumed a coarse crystalline structure, which consecutively diminished in the following order:—Samples No. 1, No. 2, No. 3, No. 4, and No. 5.

Other micro-photographs taken from polished surfaces etched by ammonia showed, amid a crystalline structure, nests of yellowish matter. Such nests are absent in samples Nos. 4 and 5, and are very marked in Nos. 1 and 2. Sample No. 5 has a remarkably fine grain, showing a very good annealing.

Science gives no means of ascertaining quite distinctly the nature of these nests. Partly, they may consist of low fusible compounds of copper with the admixed elements, and partly of cuprous oxide and other oxides, but the second supposition is less probable, as the samples contain very few impurities.

The cause of the defectiveness of these copper pipes must be assigned to the presence of oxidised compounds of

copper, which disturb the continuity of the particles of the metal, and also to the unevenness of the annealing operations, or perhaps even want of the latter. It is indispensable to insist, while ordering steam copper pipes, on very careful annealing of the finished product. Next, the melting and casting of the hollow ingots must be closely attended in order to avoid overheating of the copper, facilitating the formation of copper oxides.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JANUARY 31ST, 1905.

By SIR WILLIAM CROOKES, F.R.S.,
and
SIR JAMES DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, February 10th, 1905.

SIR,—We submit herewith, at the request of the Metropolitan Water Board, the results of our analyses of the 228 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the Metropolitan Water Board taking their supplies from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Jan. 2nd to Jan. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 228 samples examined by us during the month, all were clear, bright, and well filtered.

The rainfall measured at Oxford during January was only 0.78 inch. The average fall for thirty-five years is 2.08 inches; thus we have a deficit for the month of 1.30 inches, or 62.5 per cent below the average.

Our bacteriological examinations of 399 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 511 others from special wells, standpipes, &c., making 910 samples in all :—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	381
New River, filtered (mean of 73 samples) ..	15
Thames, unfiltered (mean of 25 samples) ..	4300
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 200 samples) ..	29
Ditto ditto ..	highest 310
Ditto ditto ..	lowest 0
River Lea, unfiltered (mean of 25 samples) ..	164
River Lea, from the East London District clear- water wells (mean of 24 samples) ..	13
Kent District, from the well at Deptford (mean of 26 samples) ..	13

Of the 323 daily samples taken from the general wells of the Metropolitan Water Board, twenty-one samples, or 6.5 per cent, were sterile. Fifteen samples, or 4.6 per cent, contained more than 100 microbes, and of these six samples contained more than 150 microbes per c.c. The fifteen excess samples contained an average of 159 microbes per c.c. In December twenty-four excess samples contained an average of 134 microbes per c.c.

The above results show that the quality of the water supplied to London during January was excellent.

In addition to the seven districts from which samples have been drawn in the past, we commenced, on the 2nd of January, to make a daily chemical and bacteriological examination of the water supplied to the Kent District. The results obtained are given in the tables.

We have also considerably extended our routine bacteriological work, as will be noticed from the increased number of samples examined.

The general condition of the Metropolitan supply continues to show that the water has been carefully filtered, and that this operation, combined with storage and aided by deficient rainfall for the time of year, has raised the purity of the London supply above the average.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

ON THE COMPLEXITY OF BERYLLIUM.

DISCUSSION.

By CHARLES LATHROP PARSONS.

Krüss and Moraht (*Liebig's Ann. Chem.*, cclxii., 47), noting the presence of a foreign substance in their ammonium carbonate solution of beryllium hydroxide, which yielded a black precipitate on treatment with ammonium sulphide, implied that a possible new element was under consideration. This claim was not directly made by them, but the fact that they stated that it yielded a black sulphide, but a white hydroxide, left no other apparent conclusion. The writer, during an extended investigation on beryllium, collected a notable quantity of this substance under conditions similar to those which obtained in Krüss and Moraht's work, and showed that it consisted almost, if not entirely, of a mixture of zinc and iron sulphides, but mainly of zinc (*Zeit. Anorg. Chem.*, xl., 407; *Journ. Amer. Chem. Soc.*, xxvi., 727). No evidence of the presence of any other substance was obtained. Pollok (*Journ. Chem. Soc.*, 1904, 604) also showed that this precipitate consisted mainly of zinc and iron, but he found also some nickel, and thought that another unknown substance might be present. His conclusions appeared shortly before my own, but did not come to my attention in time to acknowledge the fact in my paper.

Now another paper has appeared by Pollok (*Journ. Chem. Soc.*, 1904, 1630), in which he reasserts his belief that the Krüss and Moraht precipitate contains a new rare element, and claims to himself have proved the presence of another new element accompanying beryllium, evidently in large quantities, for in a single fractional sublimation made in a porcelain tube he obtained over 0.4 grm. of a chloride which, on analysis, gave an atomic weight as high as 37 for this second new element. I say second, for under no possibility could this be the same as that of Krüss and Moraht, which yielded coloured compounds, and all of which Pollok had first carefully removed by treatment with ammonium sulphide.

These results are, to say the least, startling. Pollok claims by a single re-crystallisation of the sulphate to have obtained an increase in the equivalent of the metal in the first crop of crystals over the second, in face of the fact that many previous investigators, after many re-crystallisations and rejections of the mother liquors carrying presumably the beryllium of lower atomic weight, have noticed no similar results. Also, every sublimation of the chloride gave a more volatile constituent, which must, from the analysis, contain much more than the normal equivalent of the metal, and although the removal of this metal with higher atomic weight in such large quantities would, of necessity, much reduce the atomic weight of the

true beryllium, no such result is obvious, nor are any experiments cited to show the fact. The results obtained by volatilising the chloride give a basic portion, varying in its equivalent from 4.77 to 18.74 and in the one case given re-treatment reduced the equivalent.

It is certainly to be regretted that Pollok has not given full details of manipulation, for if by any chance the gas passed through his distilling apparatus was not perfectly dry as he thought, his results are easily explained, or if his beryllium chloride was exposed to the air for even an instant in being transferred to the vessel in which it was dissolved, chlorine was almost certainly lost in the form of hydrochloric acid. Pollok speaks of "scraping out" the beryllium chloride, which would indicate that he used the same method outlined by him in a previous paper (*Trans. Roy. Soc. Dublin*, 1904, [2], viii., 150), in which the chloride was scraped from the sublimation tube into a drying bottle, inevitably coming into contact with the air of the room. In fact, he speaks of the great difficulty of transferring and weighing his chloride on account of its great hygroscopicity, and in his calculations considers the absorbed moisture which was admittedly present, but does not take into account the chief fact that this moisture immediately decomposes the chloride with certain loss of chlorine.

It has long been known that beryllium chloride is especially subject to decomposition by the slightest traces of moisture, and it is a peculiarity also of this chloride that the residue left is not affected in solubility by such action nor in any of its ordinary reactions after it is dissolved. In fact, one equivalent of hydrochloric acid will dissolve several equivalents of the basic carbonate. Also, by the action of a slight amount of moisture on the perfectly anhydrous chloride, a chloride can be obtained apparently dry, perfectly soluble, and still giving a hissing noise as it dissolves, which contains a number of equivalents of beryllium to one of chlorine. This is also true to a varying extent with the acetate, sulphate, &c., as I have elsewhere pointed out (*Zeit. Anorg. Chem.*, xlii., 254; *Journ. Amer. Chem. Soc.*, xxvi., 1437).

To properly dry a gas which is to come in contact with any of the beryllium halides and leave them unchanged is no easy problem. Even with magnesium chloride, which is much less affected than the beryllium salt, Richards has shown (*Zeit. Anorg. Chem.*, xiii., 94) that to use sulphuric acid as a desiccating agent a number of towers had to be used with fresh acid continually flowing through them. Ordinary gas drying bottles cannot safely be used for this purpose with any reagent, and calcium chloride is useless. Morley (*Am. Journ. Sci.*, xxxiv., 199; *Journ. Am. Chem. Soc.*, xxvi., 1171) has described probably the best drying apparatus known, in which phosphoric anhydride removes all but the merest traces of water. It is certain that some such appliance as this must be used if any data are to be obtained as to the beryllium equivalent from its chloride. Awdjew's high results on the chloride were undoubtedly due to the action of water, as I have already pointed out (*Zeit. Anorg. Chem.*, xl., 400; and *Journ. Am. Chem. Soc.*, xxvi., 721), he having dried his gas by calcium chloride only. Indeed, the thorough drying of the gas itself is not the only problem to be overcome, for Richards has shown that even with magnesium chloride (*Zeit. Anorg. Chem.*, xiii., 84) the sublimed salt must be sealed in a perfectly dry atmosphere before being taken from the distillation tube and precautions taken against loss of chlorine in its solution.

It will be noticed in this connection that all duplicates given by Pollok of analyses are evidently of aliquot portions of the solutions after the chloride has been dissolved, and not of separate portions of chloride dissolved separately. As none of the separate experiments give results alike, but all, without exception, yield only a chloride with a high equivalent of metal, it would certainly seem as if the trouble must be in the methods used; for otherwise the true beryllium left in his less volatile chloride must decrease in atomic weight. Until such result is

shown, and full details of manipulation given, Pollok's conclusions must be accepted with great hesitancy. If by his single re-crystallisation of the sulphate he did not succeed in removing all of the excess of sulphuric acid originally present, it is not at all surprising that his second crop of crystals yielded a lower percentage of beryllium.

It is equally impossible to discuss Pollok's spectroscopic results, for there is nothing in his paper to indicate which lines grew brighter or fainter by the separation of the new beryllium from the old. The two lines 3274 and 3247, which he does cite as belonging to some other element, are suspiciously close to two of the most prominent lines of the spark spectrum of copper, although there is nothing else to indicate that copper could be present.

I am far from stating or believing that a new element may not be present in beryl in minute quantities, but I have never seen anything to indicate it, although I have obtained results quite similar to Pollok's by the action of water on the chloride of beryllium. It is true that my work was upon an American beryl, so far as the identity of my material was known, although I used a large amount of beryllium hydroxide obtained from Kahlbaum, which may, perhaps, have come from the beryl of Limoges. The latter beryl was, however, the source of supply of many of the European investigators, and it would indeed be strange if this particular beryl contained a new element in quantities sufficiently large to increase the basic constituent six-tenths of a per cent, by a single fractional crystallisation of the sulphate, without previous discovery. Although negative results are seldom published, there can be little doubt that Nilson and Petterson also obtained results entirely similar to those of Pollok, but soon found the true explanation. They claimed that beryllium chloride also attacked glass, but overcame both difficulties sufficiently for vapour density determinations in one of their best researches, "Ueber ein neues mit exacter Temperature Bestimmung verbundenes Verfahren zur Feststellung der Dampfdichte fluechtiger Korper" (*Journ. Prak. Chem.*, [2], xxxiii., 1), which is unfortunately too little quoted. There can be no question that they and other investigators of the atomic weight of beryllium would have used the chloride but for the extreme difficulties of its manipulation, which, unconquered, always lead to results tending in the same direction as those of Pollok.

New Hampshire College, Durham, N.H.,
February 1, 1905.

ON SOME CUPRAMMONIUM SULPHATES.*

By DAVID W. HORN and EDYTHA E. TAYLOR.

(Continued from p. 78).

IV. Behaviour of the Salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ at Elevated Temperatures.

KANE has stated that when the salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ is heated at a temperature not above 149°C . it loses one-half of its ammonia and all of its water, and that the residue is an "apple-green powder" of the composition $\text{CuSO}_4 + 2\text{NH}_3$; that at temperatures not above 203°C . one-half of the remaining ammonia is lost, giving a residue of the composition $\text{CuSO}_4 + \text{NH}_3$; and that at 260°C . all of the ammonia is driven off and anhydrous copper sulphate remains.

In Kane's memoir there are the results of only three experiments upon this subject, and these we tabulate:—

Weight of salt heated.	Weight of residue.	"Parts in 100" of residue.	Percentage loss in weight by heating.	Percentage loss calculated if $\text{CuSO}_4 + 2\text{NH}_3$ is residue.
Grms.	Grms.			
1.969	1.545	78.47	21.53	21.20
4.921	3.854	78.32	21.68	
5.042	3.921	77.77	22.23	

* From the *American Chemical Journal*, xxxii., No. 3.

In this connection Kane says:—"The calculated percentage composition of ammoniacal copper sulphate is—

SO_3	32.58
CuO	32.22
2NH_3	27.89
H_2O	7.31

100.00

which is evidently transformed by heat into—

$\text{CuO} \cdot \text{SO}_3$..	64.80	HO	7.31
NH_3	13.95	2NH_3	13.94
	78.75		21.25

Thus it is demonstrated by experiment that, by the first action of heat, all of the water and half of the ammonia is driven off, and that the green residue consists of copper sulphate united with one equivalent of ammonia. . . . I have tried to separate the water without loss of ammonia by the most careful management of the flame, but could not."

It is surprising that there is in the memoir no other evidence than this of the formation and composition of what are announced by Kane to be new compounds. As has already been pointed out, losses in weight cannot be relied upon to differentiate water from ammonia. Thus, if three-fourths of the ammonia had separated from the salt at 149°C ., instead of half of it and all of the water, the loss in weight would have been 20.81 per cent instead of 21.20 per cent. It is true that Kane proved in some way, to his own satisfaction, that water is given off with the ammonia, but how he determined that *all* of the water is given off it is impossible to say. We shall show later that the same salt as that with which he was working, when heated to 100°C . instead of 149°C ., loses on the average 21.12 per cent. This percentage loss differs less from the 21.20 per cent than was his standard of reference than do his own experimental results, yet at 100°C . the salt (we shall show) loses more than half of its ammonia and probably retains a little of its water.

In discussing the change in the salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ at 203°C ., Kane gives no figures and no description of the product.

A. Behaviour of the Salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ at 149°C .—We fitted out a copper air-bath with a Reichert gas regulator so that the temperature in the bath could not rise above 149°C . We heated a specimen of the pure $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ in this bath for two hours. The product was an "apple-green powder." The following results were obtained when this product was analysed for ammonia:—

Weight of powder taken for analysis.	Weight of ammonia found.	Percentage of ammonia found.	Percentage of ammonia calculated for $\text{CuSO}_4 + 2\text{NH}_3$.
Grm.	Grm.		
0.6815	0.1130	16.58 (T)	17.61
0.6522	0.1080	16.56 (T)	
0.6516	0.1076	16.51 (T)	

Another quantity of the pure salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ was then heated in a Victor Meyer bath containing a fraction of illuminating oil boiling between 144° and 147°C . After a few hours the product was removed and analysed for ammonia and copper. It is interesting to note that the product was again of an "apple-green" colour, and that it was of a different shade of green from that produced in the former experiment. The analytical results were as follows:—

Constituent determined.	Weight of powder taken for analysis.	Weight of constituent found.	Percentage of constituent found.	Percentage calculated for $\text{CuSO}_4 + 2\text{NH}_3$.
	Grm.	Grm.		
NH_3	0.5085	0.0861	16.93 (T)	17.61
	0.5087	0.0863	16.96 (T)	
	0.4840	0.0822	16.98 (T)	
Cu	0.4597	0.1513	32.92	32.82

The insufficiency of Kane's data is emphasised by these experiments. The "apple-green powders" were mixtures whose uniformity depended upon the fact that they were stirred thoroughly during the heatings. Their composition is not even approximately represented by the formula $\text{CuSO}_4 + 2\text{NH}_3$.

No more direct way to find out just what takes place when the salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ is heated at 149°C . suggested itself than to heat weighed quantities of the pure salt under such conditions that all the water and ammonia evolved by it could be collected separately and weighed, and the residue weighed. The apparatus described for this purpose has been described on page 51. The results of four experiments, lasting two hours each, were as follows:—

Weight of salt heated.	Weight of residue after heating.	Percentage loss in weight during heating.	Weight of water collected during heating.	Percentage weight lost by salt as water.	Wt. of ammonia collected during heating.	Percentage weight lost by ammonia.
Grm.	Grm.		Grm.		Grm.	
0.6691	0.5255	21.46	0.0494	7.38	0.0953	14.24
0.5701	0.4481	21.39	0.0417	7.31	0.0807	14.15
0.5846	0.4597	21.37	0.0431	7.37	0.0828	14.16
0.5260	0.4135	21.39	0.0388	7.38	0.0745	14.16

Calculated percentage loss in weight when $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ is converted into $\text{CuSO}_4 + 2\text{NH}_3 = 21.20$.

Calculated percentage of water in the salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O} = 7.33$.

One-half the calculated percentage of ammonia in the salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O} = 13.8$.

Analyses of the residues for ammonia resulted as follows:—

Weight of residue taken for analysis.	Weight of ammonia found.	Percentage of ammonia found.	Percentage of ammonia calculated for $\text{CuSO}_4 + 2\text{NH}_3$
Grm.	Grm.		
0.2379	0.0417	17.48 (T)	17.61
0.3182	0.0552	17.35 (T)	

These experiments show that even when the salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ is decomposed in dry air at 149°C . the product is not a definite chemical compound, but a mixture that approximates in composition to the formula $\text{CuSO}_4 + 2\text{NH}_3$. This mixed product has a pale-blue colour, in no way like the "apple-green" colour of the products in the previous experiments.

B. Behaviour of the Salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ at 125°C .—A recent paper by Sabbatani that was available to us only in abstract (*Fab.*, 1897, i., 96; *Ann. Chim. Pharm.*, xxvi., 337) states that at temperatures from 120° to 125°C . both of the salts $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ and $\text{CuCl}_2 + 4\text{NH}_3 + \text{H}_2\text{O}$ lose half of the ammonia and all of the water they contain. The abstract gives no details. We carried out experiments with specimens of the first of these two salts at 120° to 125°C . in the same apparatus as those at 149°C . The results were as follows:—

Weight of salt heated.	Weight of residue after heating.	Percentage loss in weight during heating.	Weight of water collected during heating.	Percentage weight lost by salt as water.	Wt. of ammonia collected during heating.	Percentage weight lost by ammonia.
Grm.	Grm.		Grm.		Grm.	
1.2860	1.0126	21.25	0.0944	7.35	0.1812	14.09
0.6195	0.4872	21.34	0.0465	7.50	0.0868	14.01
0.5967	0.4699	21.25	0.0438	7.35	0.0811	13.59
0.4099	0.3225	21.32	0.0297	7.25	0.0558	13.63

The percentage losses are less than at 149°C ., and the product approaches in composition more nearly to the formula $\text{CuSO}_4 + 2\text{NH}_3$. The colour differed very little from that of the product at 149°C ., being slightly bluer.

(To be continued).

NOTICES OF BOOKS

Avogadro and Dalton. The Standing in Chemistry of their Hypotheses. By ANDREW N. MELDRUM, D.Sc. Edinburgh: William F. Clay. 1904.

It is difficult to give an unbiased view of this book, for the author seems to us to possess in a unique degree the faculty for exciting the antagonism of the reader, and, moreover, it is not always easy to follow his line of argument, owing to the lengthy discursive comments to which he treats his readers. His views concerning the logical development of the fundamental doctrines of chemistry are shared by many eminent men, and the fact that there are some few who, from an historical point of view, regard the importance of Avogadro's hypothesis as subordinate to that of Dalton's theory hardly seems to call for such polemical treatment in the consideration of the merits of these two great chemists. While not adding materially to what is at present known concerning the development of the hypotheses, which may be very readily gathered by judicious reading of one of the many excellent standard text-books on theoretical chemistry, the author certainly shows a wonderful fertility and resourcefulness in collecting illustrations for his arguments, as well as a thorough and far-reaching acquaintance with the literature of the subject. When confronted with such numerous quotations from various authors the reader is apt, unconsciously, to lose sight of the relative importance of their views on questions of theory, and the author frequently errs in putting before his readers as typical of a definite stage of development of scientific thought, isolated opinions which are, perhaps, purely personal, and are expressed, moreover, in somewhat ambiguous terms.

Chemistry in Daily Life. By DR. LASSAR-COHN. Translated by M. M. PATTISON MUIR, M.A. Third Edition. London: Grevel and Co. 1905.

THE third edition of the translation of these famous lectures contains some few alterations and additions, and the book still remains the most excellent example extant of a popular scientific work, in which a very difficult task is performed with the most signal success. The general reader can attack it with confidence that no part will be in any way beyond his understanding, and all classes of students will find it interesting and fascinating reading. Such books as this assist greatly in giving the student a scientific culture, and in widening his views while adding to his knowledge, and it is hardly necessary to say that the translation robs the original of none of its characteristic style, while it adapts the text to the requirements of English readers by means of explanatory notes and comments when German practice differs from that adopted in this country.

Beiträge zur Chemischen Physiologie und Pathologie. ("Contributions to Chemical Physiology and Pathology"). Band VI., 1—4 Heft. Braunschweig: Friedrich Vieweg und Sohn. 1904.

THESE issues contain an important and interesting paper, by H. Reichel and K. Spiro, dealing with the question of the loss of a ferment during, and consequent upon, its period of activity, the action of rennet being chosen as typical and convenient for practical purposes. The authors find that during the process of coagulation a loss of activity takes place, but that no appreciable part of this loss is caused by the coagulation itself. Probably during or after coagulation the rennet is divided in a definite proportion between curd and whey, which causes an apparent loss, the most probable value of the factor of distribution being 8/5.

A short paper by E. Friedmann gives a preliminary account of investigations relating to the formula of adrenalin, which have so far led the author to adopt Jowett's views on this point. A few interesting notes on the effect of radium rays on chymosin, contributed by

Signal Schmidt-Nielsen, show that very powerful radium preparations have no effect upon solutions of chymosin, even after the lapse of three months.

German Educational Exhibition, World's Fair, St. Louis, 1904: Chemistry. Berlin: W. Buxenstein. 1904.

THIS catalogue of the exhibits of the Royal Prussian Education Department in the St. Louis Exhibition contains much interesting matter, especially as regards the history of the development of the science in Germany. The catalogue was compiled by the secretary, Dr. C. Harries, to the influential committee appointed to organise and supervise the arrangements generally, and it bears very pronounced marks of its translation into the English language, which, indeed, are in some cases such as to obscure the meaning of the comments. The value of the catalogue was, however, of a hardly more than temporary nature, and no doubt it fulfilled its purpose for the benefit of visitors to the exhibition.

CORRESPONDENCE.

LICENCE FOR LABORATORY STILLS.

To the Editor of the Chemical News.

SIR,—We have in our laboratory a still for making distilled water, capacity two gallons. The Revenue Inspector has compelled us to take out a licence for this still, giving as his reason that it is too large to be exempt. We have been in several public laboratories and other places in which larger stills have been in use, and in no case have we found them paying a licence. Have we any remedy? If so, what is the best way to avoid paying? Your reply will be greatly esteemed.—I am, &c.,

G. F.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxi., No. 4, January 23, 1905.

Increase in Volume of Liquid Iron, Saturated with Carbon at the Temperature of the Electric Furnace, at the Moment of Solidification.—Henri Moissan.—The author's experiments show that pure iron contains a very small quantity of carbon during the transformation from the liquid to the solid state, and it follows the general law of solidification, its density increasing and the volume diminishing. However, when this metal is saturated with carbon at the temperature of the electric furnace, the volume, on the contrary, increases on passing from the liquid to the solid state. If the author's present series of experiments are conclusive, it shows that the electric furnace must melt the iron very quickly, and so increase the amount of carbon dissolved in the metal. The specimens of iron melted in a magnesium crucible contained less than 1 per cent of carbon, whilst if the crucible is of carbon 7.65 to 8.17 per cent will be dissolved.

A New Radiferous Mineral.—J. Danne.—The author discovers certain lead earths situated in the neighbourhood of Issy l'Éveque containing radium. The radio-active portion of these earths he finds to be a pyromorphite, some lead ores, and pegmatites, chiefly the former. The proportion of radium is variable—a ton may give about a centigram of radium bromide.

Cæsium Methylamide.—E. Rengade.—In the cold, methylamine will dissolve metallic caesium. The solution of caesium-methylammonium thus obtained rapidly decomposes, with evolution of hydrogen, giving methylamide

of caesium—a crystalline compound, very unstable, and which explodes on a rapid elevation of temperature or in contact with damp air. At a temperature of 120 it decomposes without explosion into hydrogen and caesium cyanide. Water acts upon it very slowly, producing methylamine and caesium hydrate. Up to the present time no other substitution derivative of the fatty amines with the alkaline metals have been prepared in anything like a state of purity.

Action of Pentachloride of Phosphorus on the Tertiary Cyclic Amines. Synthesis of the Dyes and Formation of Phosphorus.—P. Lemoult.—When PCl_5 acts on dimethylaniline, it gives, besides the product discovered by Michler and Walden, the leuco-base of hexamethyl violet and the two dyes which are derived from these substances; also a crystalline product very rich in phosphorus, and an orange product also rich in phosphorus; and, besides these, phosphorus itself in the white variety.

Products of Oxidation of Anthracene Octohydrate. Dihydro-oxanthranol and Hexahydroanthrone.—Marcel Godchot.—Anthracene octohydrate is rapidly oxidised by means of chromic acid, anthraquinone being formed. By careful manipulation of the reaction, intermediate oxidation products can be prepared. These correspond to anthracene hydrides and contain one or two atoms of oxygen. Amongst the oxidation products, the author was able to isolate a dihydro-oxanthranol and a hexahydroanthrone and examine their properties.

Thymomenthyl and its Derivatives.—Léon Brunel.—By applying MM. Sabatier and Senderens' method of hydrogenation to phenols, the author showed that thymol can easily be transformed into its corresponding hexahydroaromatic alcohol. He found that this reaction is the most rapid at 180°, but certain catalytic actions make it advisable to react at about 160°. Under these conditions, no appreciable quantity of acetone is produced, and the rapidity of the formation of the hexahydrothymol is scarcely diminished. An investigation of this alcohol, which the author calls thymomenthyl on account of its origin and its constitution, is the subject of the present paper.

Derivatives of Benzodihydrofurfurane.—A. Guyot and J. Catel.—It is already known that neutral phthalate of methyl and *o*-benzoylbenzoate of methyl react in a normal manner on phenylmagnesium bromide. In the present research the authors confine their attention to the ethers obtained by direct etherification of the acids in presence of hydrochloric acid. Phthalic acid and benzoyl benzoic acid are capable, under certain conditions, of giving the isomeric ethers of these acids. The authors also investigate the action of organo-magnesium compounds on these latter.

MISCELLANEOUS.

Royal Institution.—On Saturday next, February 25, at 3 o'clock, Mr. D. G. Hogarth begins a course of two lectures at the Royal Institution on "Archæology"; on Tuesday, February 28, at 5 o'clock, Prof. Karl Pearson delivers the first of three lectures on "Some Recent Biometric Studies"; on Thursday, March 2, at the same hour, Prof. H. H. Turner commences a course of three lectures on "Recent Astronomical Progress"; and on Saturday, March 11, at 3 o'clock, Prof. J. J. Thomson begins a course of three lectures on "Electrical Properties of Radio-active Substances. The Friday Evening Discourse on March 3 will be delivered by Chevalier G. Marconi on "Recent Advances in Wireless Telegraphy," on March 10 by Prof. J. J. Thomson on the "Structure of the Atom," and on March 17 by Sir Squire Bancroft on "Dramatic Thoughts: Retrospective—Anticipative." Mr. Percival Landon will give two lectures on April 4 and 11 on "Tibet"; Mr. A. Henry Savage Landor's lectures on

"Exploration on the Philippines" having been deferred until after Easter.

Society of Public Analysts.—The Annual Meeting of the Society will be held on Wednesday, March 1, at the Chemical Society's Rooms, Burlington House, Piccadilly, at 8 p.m. The Accounts for the year will be presented, the President will deliver his Annual Address, and the election of Officers and Council for the ensuing term will take place. The Ordinary Monthly Meeting of the Society will be held immediately following the Annual Meeting, when the following papers will be read:—"The Estimation of Oxygen in Copper," by S. Dickson; "Some Conditions Affecting the Ether Value of Brandies," by Philip Schidrowitz, Ph.D., and Frederick Kaye, A.R.C.Sc.; "The Determination of Higher Alcohols in Spirits," I., by Philip Schidrowitz, Ph.D., and Frederick Kaye, A.R.C.Sc.

Dr. Willy Merck.—The Medical Council of the University of Halle-Wittenberg has decided to confer the degree of M.D. *honoris causa* upon Dr. Willy Merck, in recognition of his merits in connection with *Materia Medica*. Dr. Willy Merck has charge of the manufacturing department at Messrs. Merck's Darmstadt Works, and in this capacity is intimately connected with Medicine and Pharmacy.

MEETINGS FOR THE WEEK.

MONDAY, 27th.—Society of Arts, 8. (Cantor Lecture). "Internal Combustion Engines," by D. Clerk, M.Inst.C.E.

TUESDAY, 28th.—Royal Institution, 5. "Some Recent Biometric Studies," by Prof. Karl Pearson, F.R.S.

— Society of Arts, 4.30. "The Manufactures of Greater Britain" (I. Canada), by C. F. Just.

WEDNESDAY, Mar. 1st.—Society of Public Analysts, 8. (Annual Meeting). "Estimation of Oxygen in Copper," by S. Dickson. "Some Conditions Affecting the Ether Value of Brandies," and "The Determination of Higher Alcohols in Spirits," by Philip Schidrowitz and Frederick Kaye.

— Society of Arts, 8. "The British Art Section of the St. Louis Exhibition," by Isidore Spielmann, F.S.A.

THURSDAY, 2nd.—Royal Institution, 5. "Recent Astronomical Progress," by Prof. H. H. Turner, F.R.S.

— Chemical, 8. "Latest Heat of Evaporation of Benzene and some other Compounds," by J. Campbell Brown. "Relation between Natural and Synthetic Glycerylphosphoric Acids," by F. B. Power and F. Tutin. "Reduction of Isophthalic Acid," by W. H. Perkin, jun., and S. S. Pickles. "Transmutation of Geometrical Isomers," by A. W. Stewart.

FRIDAY, 3rd.—Royal Institution, 9. "Recent Advances in Wireless Telegraphy," by Chevalier G. Marconi, D.Sc., &c.

SATURDAY, 4th.—Royal Institution, 3. "Archæology," by David G. Hogarth, M.A.

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THE CHEMICAL NEWS.

VOL. XCI., No. 2362.

POLARISED RÖNTGEN RADIATION.*

By CHARLES G. BARKLA, D.Sc., B.A., King's Coll., Cambridge,
Oliver Lodge Fellow, University of Liverpool.

EXPERIMENTS on secondary radiation from gases and light solids subject to X-rays showed that the character of this radiation differs only very slightly from that of the radiation producing it, and that the energy of this radiation is proportional merely to the quantity of matter through which a beam of Röntgen radiation of definite intensity passes, being independent of the kind of matter.

These results, and the agreement between the energy experimentally determined and that calculated, led to the conclusion that this radiation is due to what may be called a scattering of primary X-rays by the corpuscles or electrons constituting the molecules of the substance.

On the hypothesis that Röntgen rays consist of a succession of electro-magnetic pulses in the ether, each electron in the medium through which these pulses pass has its motion accelerated by the intense electric fields in these pulses, and consequently is the origin of a secondary radiation, which is most intense in the direction perpendicular to that of acceleration of the electron, and vanishes in the direction of that acceleration. The direction of electric intensity at a point in a secondary pulse is perpendicular to the line joining this point and the origin of the pulse, and is in the plane passing through the direction of acceleration of the electron.

On this theory, a secondary beam whose direction of propagation is perpendicular to that of the primary, will be plane polarised, the direction of electric intensity being parallel to the pulse front in the primary beam. If the primary beam be plane polarised, the secondary radiation from the charged corpuscles or electrons has a maximum intensity in a direction perpendicular to that of electric displacement in the primary beam, and zero intensity in the direction of electric displacement.

The secondary radiation from light substances was too feeble to allow accurate measurement of the intensity of the tertiary radiation.

A consideration of the method of production of primary Röntgen rays in an X-ray tube, however, leads one to expect partial polarisation of the primary beam proceeding from the antikathode in a direction perpendicular to that of propagation of the impinging kathode rays, for there is probably at the antikathode a greater acceleration along the line of propagation of the kathode rays than in a direction at right angles; consequently in a beam of X-rays proceeding in a direction perpendicular to that of the kathode stream there should be greater electric intensity parallel to the stream than in a direction at right angles.

Such a beam was therefore used as the primary radiation, and the intensity of secondary radiation proceeding in a direction perpendicular to that of propagation of the primary beam from a radiator placed in that beam, was studied by means of electroscopes.

In the final form of apparatus the intensity of secondary radiation was measured in two directions perpendicular to that of propagation of the primary radiation, and to each other, while the intensity of the primary beam was measured by a third electroscope.

Using paper, aluminium, or air as the radiator, as the bulb was turned round the axis of the primary beam studied, the intensity of a secondary beam was found to reach a

maximum when the direction of the kathode stream was perpendicular to that of propagation of the secondary beam, and a minimum when these two were parallel, one electroscope recording a maximum rate of deflexion when the other recorded a minimum. Many experiments were made which proved the evidence of partial polarisation conclusive.

When heavier metals, such as copper, tin, and lead, which emit a secondary radiation differing considerably in character from the primary producing it, were used as radiators, no variation in intensity of secondary radiation was observed as the bulb was rotated.

This result was not found to be affected by a considerable variation in the penetrating power of the primary radiation.

Experiments were made with several X-ray tubes.

ON MICROCOCCUS GLUTINIS: A NEW CHROMOGENIC MICROBE.

By Dr. A. B. GRIFFITHS.

CERTAIN microbes have the power of forming various pigments from the media in which they live. Each chromogenic microbe always produces the same pigment, but little is known of the chemical composition of these pigments.

The green pigment pyocyanin of Gessard has the formula $C_{14}H_{14}NO_2$. It is produced in various media by *Bacillus pyocyanus*. *Micrococcus prodigiosus* produces a red pigment which has the formula $C_{38}H_{56}NO_5$ (Griffiths, *Comptes Rendus*, cxv., p. 32). Kunz (*Monatshefte für Chemie*, ix., 361) has grown *B. pyocyanus* in nutrient gelatin kept for three or four days at the ordinary temperature, and for seven days at 35° C. The microbe liquefies the gelatin, which shows a green fluorescence, and has the odour of blue pus. Kunz extracted from the liquefied culture pyocyanin and pyoxanthose, but the liquid still showed a green fluorescence due to a distinct pigment, which is soluble in water and alcohol, and is not destroyed by boiling. This pigment is most likely produced by the oxidising action of the air on a chromogen which is formed by the bacillus, as the pigment is not contained in the bacillary cells.

Alvarez (*Comptes Rendus*, cv.) discovered the microbe which is the cause of the indigotic fermentation and production of indigo-blue. It is an encapsulated bacillus which converts indican into indigo-blue and indigluclin. *Bacterium alii*, which causes the decomposition of onions, produces a green pigment in artificial media, and there are many other microbes that produce pigments (Griffiths, *Comptes Rendus*, cx.; and the author's books, "Researches on Micro-Organisms," p. 251, and "A Manual of Bacteriology," p. 134).

The author has discovered a new microbe on glue. When ordinary glue is exposed to damp air, and in the absence of light, a whitish frothy substance sometimes makes its appearance on the surface. This substance is formed by the action of a microbe, which has been named *Micrococcus glutinis*. The organism destroys glue. When a pure culture of *M. glutinis* is made and the microbe viewed under the microscope, it presents a spherical form, and therefore belongs to the genus *Micrococcus*. It is a chromogenic microbe, and gives rise to an orange-coloured pigment when grown on gelatin, which it ultimately liquefies.

Micrococcus glutinis measures from 0.8 μ to 1 μ in diameter. It occurs singly, in twos and threes, and sometimes in chains; and it stains well with methyl violet, eosin, &c. *M. glutinis* grows well on nutrient gelatin, both as stab and streak cultures, giving rise to an orange-coloured pigment. The microbe does not appear to be pathogenic. The vitality of the micrococcus is remarkable, as it still retains its vitality when exposed, in a dry state, to a temperature of 30° C. for two months. A pure culture

* Abstract of a Paper read before the Royal Society, Feb. 16, 1903.

of it exposed to -14° C. for four days proved that it was not killed, but it was killed after twenty days' exposure at the same temperature. An E.M.F. of 6 volts killed *M. glutinis* in five minutes.

The orange-coloured pigment already referred to is soluble in ether, and only slightly soluble in alcohol. When viewed through a Zeiss micro-spectroscope, the ethereal solution (10 per cent and 1 c.m. thick) exhibits a total absorption of the blue end of the spectrum which almost reaches the Fraunhofer line F, and there is also a narrow band on the other side of F. The alcoholic extract has the same absorption spectrum but very feeble, hardly amounting to more than a faint shadow. Solutions of the pigment are optically active, hence there may be one or more asymmetric carbon atoms* in the molecule, and it proves that the *lowest* plants are capable of giving rise to asymmetric products.

The optical rotation of the pigment in ether was found to be -2.5° , and the specific rotatory power was ascertained by using Landolt's formula. A determination of the specific rotation, using a solution (specific gravity of the solution = 0.92) containing 2.02 grms. of pigment in 100 c.c. of ether in a 2-decimetre tube, gave as the mean of four readings an angle of -2.5° . Hence the specific rotation:—

$$[\alpha]_D = \frac{100 \times 2.5}{2.02 \times 2 \times 0.92} = -68^{\circ} 75' \text{ at } 17^{\circ} \text{ C.}$$

The empirical formula of the orange pigment has been ascertained. The pigment was freed from fatty bodies by treating its ethereal solution with a solution of sodium hydroxide (N/100), and subsequently separating the two liquids. The ethereal solution was carefully evaporated to dryness, and the residue dissolved in pure ether, and again evaporated to dryness. Analyses of the pigment gave the following results:—

I.	{ Pigment used (grm.)	0.1165
	{ CO ₂ produced (grm.)	0.2300
	{ H ₂ O produced (grm.)	0.0501
II.	{ Pigment used (grm.)	0.12915
	{ Nitrogen produced (c.c.)	5.15
	{ Temperature (C.)	16°
	{ Pressure (m.m.)	748

	Found.		Calculated for C ₁₄ H ₁₅ NO ₇ .
	I.	II.	
Carbon	53.84	—	54.36
Hydrogen	4.77	—	4.85
Nitrogen	—	4.57	4.53
Oxygen	—	—	36.26

The above figures correspond with the formula C₁₄H₁₅NO₇.

The electrical resistances of selenium determined by the Wheatstone bridge method, and then exposed to ethereal solutions of the pigment for fifteen minutes at a distance of 5 c.m., gave the following results:—

Solutions of the pigment.	Resistances (in ohms) of selenium before exposure.	Resistances (in ohms) of selenium after exposure.
I.	360,000	350,000
II.	382,000	360,000
III.	404,000	368,000

As light radium rays and Röntgen rays produce a reduction of the resistance of selenium, these investigations appear to show that solutions of the pigment emit rays.

Phosphorescence has been observed in many plants (Griffiths, *Berichte*, xxxvi., 3959; *Comptes Rendus*, cxxxvi.; *CHEMICAL NEWS*, vol. lxxxviii., p. 249), and in some animals; and Mr. T. A. Edison has proved that

chlorophyll, curcumine (from turmeric), and daturine (from *Datura Stramonium*) give rise to phosphorescence.

Radio-activity appears to be a universal property; as radio-active emanations exist in the atmosphere, in soil, in certain waters, and in plants and animals.

PERCHROMIC ACID AND THE PERCHROMATES.*

By HORACE G. BYERS, University of Washington,

and
E. EMMET REID, Baylor University, Texas.

Historical.

THE well-known blue compound, formed when solutions of chromic acid or acidified chromates are treated with hydrogen peroxide, was discovered by Barreswill in 1847 (*Ann. Chim. Phys.*, [3], xx., 2641), and is in common use as a means of detection of both chromic acid and hydrogen peroxide because of the intense blue colour of its solution in ether, in which it is comparatively stable. The discoverer assigned to this compound the formula Cr₂O₇, because of the volume of oxygen evolved by it when reacting with hydrogen peroxide. He was unable to obtain any stable compounds of alkalis with it, nor was he able to isolate the substance giving rise to the blue colour.

Fairley, by similar means, deduced the formula CrO₆ for the blue substance (*CHEMICAL NEWS*, xxxiii., 237).

Moissan obtained the blue compound from the ethereal solution by rapid evaporation at -20° as any oily liquid, and showed that in this condition it evolved hydrogen by action on sodium amalgam (*Comptes Rendus*, cxvii., 96). From the amount of oxygen which the blue solution evolved by its spontaneous decomposition in the presence of alkalis, he concluded that the blue substance has the composition CrO₃.H₂O₂. He states that by its action on the alkali metals chromates are produced.

Berthelot, studying the compound from the point of view of the oxygen evolved when acidified bichromates are treated with hydrogen peroxide, assigns to the blue compound the probable formula H.CrO₄.H₂O₂ (*Comptes Rendus*, cviii., 25; clvii., 477).

Pechard, by treatment of the aqueous solution of the blue compound with barium hydroxide, obtained a compound to which he assigns the formula BaCrO₅ (*Comptes Rendus*, cxiii., 39).

Hausserman, by treatment of chromium hydroxide with sodium peroxide, obtained a compound to which he assigns the formula Na₆Cr₂O₁₅.28—30H₂O (*Fourn. Prakt. Chem.*, xlviii., 70).

Wiede prepared from the blue ethereal solution a salt to which he gave the composition (NH₃)₃CrO₄, and a series of salts of the organic bases to which he assigns the general formula RCrO₅ (*Ber.*, xxx., 2178; xxxi., 516, 3139; xxxii., 378). He also prepared the salts of ammonium, sodium, and potassium, and assigns to these the composition expressed by the formula MCrO₅.H₂O₂. He concludes, therefore, that the blue solution contains chromium in the state of oxidation implied by the formula Cr₂O₉.

Patten, by reason of the colour produced when the blue aqueous solution is treated with a solution of sodium acetate, and because of a purple precipitate formed when the ethereal solution is treated with solid sodium acetate, concludes that the blue solution contains chromium in the state of oxidation conforming to the oxide CrO (*Am. Chem. Journ.*, 1903, xxix., 385).

A study of the foregoing literature convinced the authors of the present paper that more work on this subject is desirable, and that the many attempts to get compounds of the blue substance by direct treatment with the alkali metals failed only by reason of the temperature at which

* Concerning asymmetric carbon atoms, vide two important papers on the subject:—(a) Crum Brown in *Revue Française d'Edimbourg*, 1897; and (b) F. R. Japp in *The British Association Report*, 1898.

* This work was begun at the University of Washington, and continued, jointly, at the University of Chicago, in the laboratory of General and Physical Chemistry. From the *American Chemical Journal*, xxxii., No. 5.

these attempts were made. The following investigation resulted :—

Experimental.

The Potassium Salt.—Acting on the hypothesis that the formation of chromates by the action of alkalis and the alkali metals is due to the decomposition of the product first formed, the blue solution was prepared, using an acidified bichromate solution saturated at the ordinary temperature of the room, and just sufficient 2·5 per cent hydrogen peroxide to give the supernatant layer of ether an intense blue colour. This blue solution was cooled to about -20° and freshly cut pieces of potassium dropped in. The low temperature was maintained by the use of solid carbon dioxide, which was placed in an ether-bath surrounding the blue solution, or was dropped directly into the latter. A vigorous evolution of gas, which was proved by analysis to be hydrogen, followed the addition of the potassium. At the same time there was produced a purplish-black precipitate, and the blue solution was ultimately decolourised. This precipitate quickly decomposes, when exposed to the air at the room temperature, with the evolution of oxygen and the formation of a substance which proved to be the bichromate. It dissolves in water with the formation of a sherry wine colour, and, if the water is ice-cold, only slowly fades to the colour of the chromate. It regenerates the blue colour when acidified in the presence of ether.

As the compound seems to begin to decompose even below zero the analysis by the usual methods is difficult. Since the compound evolves oxygen on decomposition and forms a dichromate, it was thought that the determination of the available oxygen would be a means of arriving at the composition.

A N/10 solution of potassium bichromate was titrated against a neutral solution of ferrous ammonium sulphate of similar concentration. Measured quantities of the latter, usually 50 c.c., were diluted with about 100 c.c. of recently boiled water. In the earlier experiments ordinary distilled water was used. Into the iron solution, portions of the potassium salt were dropped, and the solution vigorously stirred. The portions used were washed with cold ether, and care was taken to ensure a large excess of iron. The solution was acidified with sulphuric acid, and the excess of iron determined by titration against the bichromate solution, using ferricyanide as an indicator.

The titrated solution was then made alkaline with ammonia, boiled, and filtered. The precipitated hydroxides of iron and chromium were dried and fused in an iron crucible with an excess of sodium peroxide and a small piece of potassium hydroxide over a Bunsen burner. The fused mass was dissolved in water, saturated with carbon dioxide, and filtered. The residue was again fused and re-dissolved. The two solutions were titrated against the iron solution. These titrations give, in the first instance, the oxidising power of the potassium salt, and in the second, the oxidising power of its chromium in the known form of the chromate. Of course, deduction was made for the amount of chromium introduced in the first titration.

The following results were obtained, the oxidising power being expressed in terms of c.c. of N/10 bichromate. The ratio given in the tables is based on the following considerations :—In the iron solution, when acidified, the chromates are reduced to the state of oxidation represented by the oxide Cr_2O_3 . In the case of the chromate this is

represented by $2\text{CrO}_3 \rightarrow \text{Cr}_2\text{O}_3 + 3\text{O}$. If the state of oxidation of the chromium in the blue compound corresponds to the oxide Cr_2O_7 the relation would be $\text{Cr}_2\text{O}_7 \rightarrow \text{Cr}_2\text{O}_3 + 4\text{O}$. The ratio of the available oxygen would then be 4 : 3.

A solution of potassium hydroxide in ether will also precipitate the potassium salt, and determination of the potassium chromate ratio was made upon two samples of the partially dried salt so prepared, with the following results. The potassium was weighed as the sulphate and the chromium as the oxide :—

TABLE II.

	Salt.	Potassium.	Chromium.	Ratio of K : Cr.
	M.grms.			
1	122	24·6	34·4	1 : 1·38
2	127	27·3	37·7	1 : 1·39
	Calculated			1 : 1·33

Wiede (*loc. cit.*) prepared, in the same way, a salt very similar in appearance to the one under investigation, and ascribed to it the formula $\text{KCrO}_5 \cdot \text{H}_2\text{O}_2$. He also prepared his salt by precipitation of the blue solution with an alcoholic solution of potassium cyanide. In this salt he continually found the ratio of potassium to chromium as expressed above, but the oxygen values were higher than those obtained by us. He prepared his blue solution by use of a very large excess of hydrogen peroxide, 250 c.c. of a 10 per cent solution with 10 grms. of chromic anhydride.

It seemed probable that the difference in results is in some way connected with this excess of hydrogen peroxide. To test this point Wiede's salt was prepared, and instead of using his method of analysis the oxidising power of the salt was determined as previously outlined. The result is given in Table III. The blue solution was then prepared without excess of hydrogen peroxide, and the additional precaution was taken of washing the solution twice with a chromic acid solution. The results in this case are given in Table IV.

TABLE III.

	Salt.	Chromate.	Ratio.
1	35·0	22·9	4·58 : 3
2	26·5	17·4	4·57 : 3
3	17·3	11·4	4·56 : 3

A second sample :—

1	37·3	24·10	4·66 : 3
2	35·15	22·11	4·77 : 3
3	29·85	19·9	4·49 : 3

TABLE IV.

1	16·9	12·8	3·96 : 3
2	11·1	8·14	3·96 : 3
3	16·2	12·12	3·98 : 3

It seems possible that the large amounts of oxygen indicated in Table III. are due to cryoscopic hydrogen peroxide or to the formation of a compound of another series (see summary at close of article). An attempt was made to obtain a complete analysis of the potassium salt by the following method :—Portions of the same sample of the potassium salt used in the analyses given in Table IV. were dropped into tubes, the lower closed ends of which were surrounded with solid carbon dioxide. The upper ends were then sealed with a blast-lamp. Thus enclosed, the substance changes quietly into the bichromate. On opening these tubes, after weighing, considerable gas escaped, and the odour of ether was plainly noticeable. Tubes 1 and 1 (see Table V.) were opened by breaking off the capillary tips by means of an iron rod passing through the stopper of a U-tube in which they were successively placed. The U-tube was immersed in a boiling salt solution, and the water from the tubes driven over into weighed calcium chloride tubes by means of carbon dioxide. In tubes 3 and 4 the moisture was determined

TABLE I.

	Salt solution.	Chromate solution.	Ratio.
	C.c.	C.c.	
1	50·5	39·5	3·84 : 3
2	27·4	19·4	4·24 : 3
3	27·4	19·9	4·14 : 3
4	34·1	25·4	4·03 : 3
5	29·5	21·75	4·07 : 3
Mean			4·065

by weighing the tubes after opening, and again after heating to 140° in an air-bath. The contents of each tube were washed into a platinum dish and titrated with the iron solution, the chromium and iron precipitated, and the potassium determined as the sulphate. The chromium precipitate was fused and determined as usual. The results follow. The excess of potassium in 1 and 2 over that required for the bichromate is probably due to potassium cyanide, or to potassium carbonate contained in the cyanide used.

TABLE V.

	I.	II.	III.	IV.
Total substance	70.5	57.9	—	49.17
Weight of gas.. ..	9.19	10.9	—	11.6
Weight of moisture	4.11	2.9	4.3	2.4
Weight of solid contents ..	56.5	44.1	55.3	35.7
Weight of bichromate (by titration)	52.9	40.5	53.18	33.19
Weight of bichromate (by fusion)	52.7	41.2	53.8	34.1
Potassium found	17.1	14.3	14.1	8.84
Calculated potassium (from bichromate found)	14.1	10.7	14.3	8.89

The above results make it clear that the substance yields pure potassium bichromate on spontaneous decomposition, and that the potassium and chromium are present in the same ratio as in the dichromate.

(To be continued).

ON SOME CUPRAMMONIUM SULPHATES.*

By DAVID W. HORN and EDYTHA E. TAYLOR.

(Continued from p. 94).

IV. Behaviour of the Salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ at Elevated Temperatures (continued).

C. Behaviour of the Salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ at 100°C .—We noticed that this salt is decomposed also at 100°C . When heated in dry air at 100°C , a product having constant weight is finally obtained. The following results show this, and, incidentally, the accuracy associated with all the experiments in this paper that involve the weighing of boats and residues:—

	Grms.
6. Total weight (tube, boat, and residue)	10.39500
Weight after twelve hours more at 100°C ..	10.39358
Weight after twenty hours more at 100°C ..	10.39359
Weight after thirty-six hours more at 100°C ..	10.39351
7. Total weight (platinum boat and residue) ..	1.16791
Weight after three hours more at 100°C ..	1.16791
8. Total weight (platinum boat and residue) ..	1.21362
Weight after six hours more at 100°C ..	1.21363

Repeated experiment showed that the losses in weight are not always the same. This is readily seen from the following figures:—

Number of experiment.	Weight of salt heated. Grm.	Weight of residue after heating. Grm.	Percentage loss in weight.
1.	0.4894	0.3878	20.75 (T)
2.	0.4564	0.3606	20.99
3.	0.4164	0.3273	21.39 (T)
4.	0.4664	0.3669	21.33
5.	0.4332	0.3410	21.28 (T)
6.	0.4184	0.3300	21.24

The analyses of the products in these experiments indicated that they were of varying composition:—

Con-stituent determined.	Weight of residue taken for analysis. Grm.	Weight of constituent found. Grm.	Percentage of constituent found.
NH_3	0.8167	0.1358	16.62 (T)
	0.2201	0.0368	16.72 (T)
	0.1911	0.0324	16.83 (T)
	0.2393	0.0394	16.48 (T)
Cu	0.2311	0.0741	32.07
	0.1873	0.0602	32.18
	0.2215	0.0896	32.23

Latschinoff has stated that when hydrochloric acid is led over pentahydrated copper sulphate at room temperature there results by degrees the compound $\text{CuSO}_4 + 5\text{H}_2\text{O} + 3\text{HCl}$, and by further action the compound $\text{CuSO}_4 + 2\text{H}_2\text{O} + 2\text{HCl}$, which breaks down when air is led over it into $\text{CuSO}_4 + \text{H}_2\text{O} + \frac{1}{2}\text{HCl}$. This $\frac{1}{2}\text{HCl}$ cannot be removed by a stream of air. He has also stated that when the compound $\text{CuSO}_4 + 5\text{NH}_3$ is heated under certain conditions the final product is $\text{CuSO}_4 + \frac{1}{2}\text{NH}_3$. Evidence of this kind is of especial interest as bearing upon the molecular weight of (solid) copper sulphate. At first we believed that the residue we obtained at 100°C . might be classed with these interesting compounds. Thus, if the product was fairly represented by the formula $\text{CuSO}_4 + \frac{1}{2}\text{NH}_3 + \frac{1}{2}\text{H}_2\text{O}$, it would be formed from the salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ by a loss of 21.15 per cent, and it would contain 16.50 per cent ammonia and 32.79 per cent copper. The experimental results that have been given do not quite agree with these calculated values, but approximate to them. This might be due to the water evolved from some of the salt acting upon those, or other, parts of the specimen producing mixed products. To avoid this as far as possible, we heated very small quantities of pure $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$, carefully spread out in thin layers on the bottom of a thin platinum boat. This boat was used to distribute better the error in weighing. The following results were thus obtained:—

Number of experiment.	Weight of salt heated. Grm.	Weight of residue after heating. Grm.	Percentage loss in weight.
7.	0.0682	0.0537	21.21
8.	0.1261	0.0996	20.96
9.	0.1112	0.0877	21.08
10.	0.1746	0.1377	21.15
11.	0.1617	0.1276	21.09
12.	0.2644	0.2085	21.12

Several of the residues were analysed:—

Number of expt.	Con-stituent determined.	Weight of residue taken for analysis. Grm.	Weight of constituent found. Grm.	Percentage of constituent found.	Percentage of constituent calculated for $\text{CuSO}_4 + 2\text{NH}_3$
9.	Cu	0.0870	0.0281	32.29	32.82
10.		0.1373	0.0447	32.58	
11.		0.1275	0.0418	32.76	
12.	NH_3	0.2084	0.0365	17.49	17.61

These results are not in agreement with the formula we have tentatively assumed. If the product could be correctly represented by the formula $\text{CuSO}_4 + \frac{1}{2}\text{NH}_3 + \frac{1}{2}\text{H}_2\text{O}$, its formation should be preceded by a loss in weight of 21.12 per cent, whereas the average of these last six experiments is 21.10 per cent. But this formula requires 15.39 per cent ammonia.

It is not possible to find any one formula to fit all the data at hand. Whatever may be the case in other instances, our experiments leave no doubt that at 100°C . $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ yields a mixed residue.

We believe that the action of water is responsible for the production of these mixtures. We tested this by heating the salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ at 100°C . in a bath where the vapour of water had access by free diffusion to the heated material. The material in the bath was stirred

* From the *American Chemical Journal*, xxxii., No. 3.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, February 15th, 1905.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

MR. A. W. HENZELL was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Arthur Amos, B.A., Spring Grove, Wye, Kent; William Morris Colles, jun., B.Sc., 16, Birchington Road, West Hampstead, N.W.; Miles Coupe, 46, Millarborn Lane, Waterfoot, near Manchester; John William Taylor, University College, Reading.

It was announced that the following changes in the Officers and Council were proposed by the Council:—

As President: Prof. R. Meldola, F.R.S., *vice* Prof. W. A. Tilden, F.R.S.

As Vice-Presidents: Prof. A. Smithells, F.R.S., and Prof. W. P. Wynne, F.R.S., *vice* Prof. P. F. Frankland, F.R.S., and Prof. R. Meldola, F.R.S.

As Secretary: Prof. A. W. Crossley, *vice* Prof. W. P. Wynne, F.R.S.

As Ordinary Members of Council: Mr. E. C. C. Baly, Dr. G. T. Moody, Mr. W. J. Sell, F.R.S., and Dr. J. Wade, *vice* Dr. A. Harden, Dr. J. T. Hewitt, Dr. C. A. Kohn, and Dr. S. Ruhemann.

Mr. E. Grant Hooper, Dr. H. F. Morley, and Dr. J. Wade were elected to audit the Society's accounts.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—
 Andrea Angel, M.A.; Francis William Fredk. Arnaud; James Henry Ashwell; James Hector Barnes, B.Sc.; Samuel Henry Clifford Briggs, B.Sc.; James H. Campbell; Hem Chandra Chatterji, B.A.; F. E. Clarke, Ph.D., B.Sc.; George Douglas Clarkson; Bernard Collett; Samuel George Eade; Charles Richard Gardner; Herbert Goodier; Frederick William Heely; James Alexander Russell Henderson, B.Sc.; Carl Richard Hennings, Ph.D.; Bernard Mount Jones, B.A.; Percy Walter Jones; Tudor Foulkes Jones, B.Sc.; Herbert Louis Leech; Joseph Lister, B.Sc.; George Moss Lloyd, M.A., M.Sc.; Edward William Lucas; Alfred Courtenay Luck; Andrew Norman Meldrum, D.Sc.; William Sloan Mills, M.A.; Charles Watson Moore, B.Sc.; Thomas Pennycuik, B.Sc.; Bert Perrott; Frank Lee Pyman, B.Sc., Ph.D.; Ernest Quant; William Henry Ratcliffe, B.Sc.; Frederick George Richards; Harold Rudolph Rogers, B.A.; Fred Scholefield, B.Sc.; Harold Schröder; John Irwin Scott, B.A.; William Dunham Seaton; William Herbert Simmons, B.Sc.; Gustav Arthur Troye; William Phillip Want; Eric H. Weiskopf; Ernest Wheeler; John Henry Becker Wigginton; John Wells Wilkinson, M.A.; Alan Herbert Williams.

Of the following papers, those marked * were read:—

*16. "Nitrogen Halogen Derivatives of the Aliphatic Diamines." By FREDERICK DANIEL CHATTAWAY.

Although the quinonedichloroimides, obtained from the aromatic diamines, were among the earliest studied nitrogen halogen compounds, no derivatives of the aliphatic diamines have hitherto been described. Both the diamines themselves and the diacyldiamines, however, readily yield such substances in which the whole of the hydrogen attached to nitrogen is replaced by halogen, and a number of such derivatives of ethylenediamine and trimethylenediamine have been prepared. The most noteworthy of the compounds described were ethylenetetrachlorodiamine, $\text{NCl}_2\text{CH}_2\text{CH}_2\text{NCl}_2$, and ethylenetetrabromodiamine, $\text{NBr}_2\text{CH}_2\text{CH}_2\text{NBr}_2$; both are stable substances, the former a liquid giving off peculiarly irritating vapours, the latter a well crystallised solid.

*17. "The Nitration of Substituted Azophenols." By JOHN THEODORE HEWITT and HERBERT VICTOR MITCHELL.

The authors have systematically studied the action of dilute nitric acid and of a mixture of concentrated nitric and sulphuric acids on the three nitrobenzeneazophenols. With dilute nitric acid, substitution takes place in the ortho-position with respect to the hydroxyl group in each case (compare *Trans.*, 1900, lxxvii., 99; 1901, lxxix., 49, 155); it is, however, remarkable that the concentrated mixed acids have the same effect.

This result contradicts Noelting's statement (*Ber.*, 1887, xx., 2997) to the effect that if benzeneazophenol is dissolved in concentrated sulphuric acid and treated with one molecule of nitric acid, *p*-nitrobenzeneazophenol results; whilst with two molecules of nitric acid a product is obtained identical with that derived from the diazotisation of 2:4-dinitroaniline and subsequent coupling with phenol.

Whilst Noelting is correct in stating that the first nitro-group enters the benzene nucleus in the para-position with respect to the azo-group, he is obviously wrong as to the position assumed by the second nitro-group, since *p*-nitrobenzeneazophenol, when dissolved in concentrated sulphuric acid, and treated with one molecular proportion of nitric acid, furnishes a product which melts at the same temperature, and does not depress the melting point of the product of coupling *p*-nitrophenyldiazonium salts with *o*-nitrophenol.

The evidence as to the constitution of the product obtained by nitrating *m*-nitrobenzeneazophenol is as follows:—(i.) The same product is obtained by nitration with strong and dilute acids, (ii.) it has the same melting point as the product obtained by the action of strong sulphuric acid on 3:3'-dinitroazoxybenzene.

o-Nitrobenzeneazo-*o*-nitrophenol (m. p. 187°) has been obtained not only by nitration of *o*-nitrobenzeneazophenol, but also by coupling *o*-nitrophenyldiazonium sulphate with *o*-nitrophenyl; its *acetyl* and *benzoyl* derivatives melt at 119° and 174° respectively.

m-Nitrobenzeneazo-*o*-nitrophenol melts at 179°; its *acetyl* and *benzoyl* derivatives melt at 138° and 169° respectively.

p-Nitrobenzeneazo-*o*-nitrophenol melts at 212° (Noelting gives 200°); its *acetyl* and *benzoyl* derivatives melt at 138° and 179° respectively.

2-Nitrotoluene-4-azophenol melts at 186°, its *acetyl* derivative at 113°. 3-Nitrotoluene-4-azophenol melts at 158°.

The last two azo-compounds have been obtained by coupling the diazotised nitro-*p*-toluidines with phenol, but not by nitrating *p*-tolueneazophenol.

*18. "The Estimation of Saccharin." By CHARLES PROCTOR.

The "sulphate" and "salicylic acid" methods of estimating saccharin are troublesome, and require great attention to details in order to obtain satisfactory results.

The process described by E. Emmet Reid (*Am. Chem. Journ.*, 1899, xxi., 461) for the estimation of real saccharin (*o*-benzoisulphinide), by boiling with dilute acid (which hydrolyses this compound to the acid ammonium salt of sulphenbenzoic acid), and then distilling off and estimating the ammonia so produced, has been tested and found to be convenient and reliable.

The paper also describes a simple volumetric process by means of which the combined percentage of real saccharin (*o*-benzoisulphinide) and *p*-sulphamidobenzoic acid in commercial samples and mixtures containing saccharin can be readily determined. This process depends on the liberation of iodine by both real saccharin and *p*-sulphamidobenzoic acid, when either or both are mixed with a solution containing potassium iodide and iodate.

By a combination of this "iodine process" with the "ammonia process," the separate percentages of "para-" and "ortho-saccharin" can be readily determined, and then indirectly that of any unaltered sulphonamide, &c.

19. "The Analysis of Samples of Milk Referred to the Government Laboratory in connection with the Sale of Food and Drugs Acts." By THOMAS EDWARD THORPE.

In connection with the administration of the Sale of Food and Drugs Acts, samples of milk are frequently referred by magistrates to the Government Laboratory for examination. These referred samples are invariably sour when received, and it is therefore of importance to determine whether this fact prevents a true inference as to the character of the fresh milk, or interferes with the determination of the degree of sophistication to which the milk may have been subjected.

The charges usually brought against milk by public analysts are that it has been mixed with water, or that fat has been abstracted. The proof or disproof of the allegation depends upon a determination in the sample of the amount of fat and of the non-fatty solids.

As regards the fat, it would appear that bacteria producing steatolytic enzymes do not develop to any considerable extent in sour milk. Direct experiments show that any action they may produce is too inconsiderable to affect to any substantial extent the experimental proof of the validity of any charge based upon an alleged deficiency in fat.

As regards a charge based upon an alleged deficiency of non-fatty solids, as the aggregate weight of the non-fatty solids is affected to some extent by the fermentative changes associated with the souring, it has been necessary to examine these changes in some degree of detail with a view to ascertain their bearing upon the experimental facts needed to establish the inference of sophistication, and to determine its extent.

This communication contains the results of such an examination. It serves to establish the character of the products of the change in so far as they affect the quantitative results, describes how they may be determined, and what is the nature and amount of the correction needed to account for the slight loss in the non-fatty solids which generally results on keeping the milk.

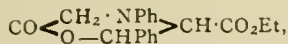
20. "The Condensation of Anilinodiacetic Esters in presence of Sodium Ethoxide." By ALFRED THEOPHILUS DE MOUILPIED.

The esters and half-esters of anilino- and toluidino-diacetic acids and anilinoacetylpropionic acid and certain of its esters were prepared and condensed either alone or in the presence of benzaldehyde or ethyl oxalate by means of sodium ethoxide.

Sodium ethoxide does not bring about ring formation in the case of the anilinodiacetic esters, these substances behaving like glutaric esters.

Ethyl anilinoacetylpropionate loses one molecule of alcohol, and gives ethyl phenyloxypyrrrolinocarboxylate; this ester on saponification gives the acid, which in its turn loses carbon dioxide on heating. In alcoholic solutions, sodium ethoxide only saponifies the esters.

With benzaldehyde, ethyl anilinodiacetate condenses to a lactone having the constitution—



which yields the acid on saponification.

Alcoholic solutions of anilino- and toluidino-diacetic esters, when treated with ammonia, yield the corresponding diamides.

Sodium ethoxide readily brings about a condensation between ethyl anilinodiacetate and ethyl oxalate, yielding a substance having very different properties from the ketopentamethylene derivatives obtained by Dieckmann with ethyl glutarate. The product has the composition $\text{C}_{16}\text{H}_{17}\text{O}_6\text{N}$, and probably a quinonoid structure. On using methyl oxalate, a different compound was obtained, as also on substituting sodium methoxide for the ethoxide. Similar experiments were carried out with methyl anilinodiacetate.

21. "The Basic Properties of Oxygen at Low Temperatures; Additive Compounds of the Halogens with Organic Substances Containing Oxygen." By DOUGLAS MCINTOSH.

It was previously shown (Walker, McIntosh, and Archibald, *Trans.*, 1904, lxxxv., 1098; Archibald and McIntosh, 1904, lxxxv., 919) that organic compounds containing oxygen united at low temperatures with the halogen hydrides to form definite compounds. Continuing these low temperature experiments with chlorine and bromine, the following compounds were made:—

	M. p.		M. p.
CH_3OBr	-55°	$\text{CH}_3 > \text{COCl}_2$	-53°
$\text{C}_2\text{H}_5\text{OBr}$	-61°	$\text{CH}_3 > \text{CO} \cdot \text{Br}_3$	-12°
$\text{C}_2\text{H}_5 > \text{OCl}_2$	-51°	$\text{CH}_3 \cdot \text{CO}_2(\text{C}_2\text{H}_5)\text{Cl}_3$	-64°
$\text{CH}_3 > \text{OBr}_2$	-68°	$\text{CH}_3 \cdot \text{CO}_2(\text{C}_2\text{H}_5)\text{Br}_3$	-39°
$\text{CH}_3 > \text{OBr}_2$	-40°	$(\text{CH}_3 \cdot \text{COH})_3\text{Cl}_2(?)$	-11°

These formulæ must, in some cases, be doubled in order to represent the constitutions of the compounds with oxygen as a quadrivalent element.

These substances are formed with the evolution of a small amount of heat, have definite melting points, and crystallise in needles or prisms. At a low temperature (-80°), there is no substitution, and only additive compounds are produced.

Compounds of chlorine with the alcohols and with methyl ether were not obtained, but would doubtless crystallise out at a lower temperature. Compounds were made with the halogens and acetic acid, but difficulty was experienced in preventing the acetic acid from being precipitated, so that the analyses varied widely, and showed a large amount of acid present. The halogens form compounds with acetaldehyde, but these are quickly decomposed, and a mixture of meta- and para-acetaldehydes results. Iodine is the most powerful of the halogens in bringing about this change, whereas chlorine is the least.

22. "Organic Derivatives of Silicon." By FREDERIC STANLEY KIPLING.

The continuation of this work (*Proc.*, 1904, xx., 15), in which the author has been assisted by Mr. A. Hunter, has led to the preparation of a number of compounds of which the following is a brief preliminary account; for the purpose of systematic nomenclature, these compounds may be conveniently regarded as derivatives of *silicane*, SiH_4 , or of *silicol*, SiH_3OH .

Diphenylethylchlorosilicane, SiEtPh_2Cl , is obtained as a by-product in the preparation of phenylethylchlorosilicane (phenylethylsilicon dichloride); it is a fuming liquid boiling at about 240° (115 m.m.).

Phenylethylpropylchlorosilicane, SiEtPrPhCl , is the principal product of the interaction of phenylethylchlorosilicane and magnesium propyl bromide; it boils at about 255°, but has not been obtained quite free from impurity.

Phenylmethylethylpropylsilicane, SiMeEtPrPh , is obtained when the preceding compound is treated with magnesium methyl iodide; it is a mobile liquid, boiling at 229–231°, and is decomposed by sulphuric acid, giving, apparently, benzene and *methylethylpropylsilicol*, SiMeEtPrOH .

Phenylbenzylethylpropylsilicane, SiEtPrPhBz , prepared from magnesium benzyl chloride and phenylethylpropylchlorosilicane, is a colourless liquid, boiling at 249–251° (100 m.m.), and is readily decomposed by sulphuric acid, giving benzene and *benzylethylpropylsilicol*, SiEtPrBzOH , or the corresponding *ether* ($\text{SiEtPrBz}_2\text{O}$).

When this decomposition product of phenylbenzylethylpropylsilicane is heated with sulphuric acid, it undergoes sulphonation, giving apparently various acids of which hitherto only one has been isolated. This compound seems to be *benzylethylpropylsilicolsulphonic acid* and has apparently the composition $\text{SiEtPr}(\text{OH}) \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$,

but it may be derived from the corresponding ether (see below); its ammonium salt crystallises well in colourless plates and is very readily soluble in water; its barium salt separates from aqueous alcohol in well defined crystals and is almost insoluble in water; its 1-methylamine salt crystallises well from aqueous alcohol and melts at about 230° ; its boronamine salt also crystallises well and melts at about 211° ; the salts of most of the alkaloids do not crystallise readily.

Benzylethylchlorosilicane, SiEtBzCl_2 , prepared by treating ethyltrichlorosilicane with magnesium benzyl chloride, is a colourless, fuming liquid boiling at $168-170^{\circ}$ (100 m.m.), and is separated from the other products of higher boiling point, which no doubt contain *dibenzylethylchlorosilicane*, SiEtBz_2Cl , by fractional distillation; it is decomposed by water giving the corresponding silico-ketone, *benzylethylsilicane*, SiEtBzO , a colourless oil.

Benzylethylpropylchlorosilicane, SiEtPrBzCl , is obtained by the interaction of the preceding compound and magnesium propyl bromide; it boils at about $194-196^{\circ}$ (100 m.m.), but is not easily obtained in a state of purity. When decomposed with water, it gives two compounds, one of which, probably the ether $(\text{SiEtPrBz})_2\text{O}$, boils at about 255° (25 m.m.); the principal product, however, is *benzylethylpropylsilicilol*, SiEtPrBzOH , a colourless, mobile liquid which boils at about 155° (25 m.m.).

This alcohol is readily sulphonated, giving apparently at least two sulphonic acids, one of which has been isolated in the form of its salts and found to be identical with the compound described above, which is obtained from the decomposition product of phenylbenzylethylpropylsilicane.

This fact seems to prove that the sulphonic acid in question is, as stated, a derivative of benzylethylpropylsilicilol, but molecular weight determinations made with its ammonium salt indicate that polymerisation or condensation has occurred.

Benzylmethylpropylsilicane, SiMeEtPrBz , is formed when benzylethylpropylchlorosilicane is treated with magnesium methyl iodide; it is a mobile liquid boiling at about 250° .

The main object of this investigation being the preparation of an optically active compound containing an asymmetric silicon group (compare Kipping and Lloyd, *Trans.*, 1901, lxxix., 449), most of the work described in this note is of a preliminary character, and the intermediate compounds have not yet been carefully examined.

23. "Photographic Radiation of some Mercury Compounds." By ROBERT DE JERSEY FLEMING-STRUTHERS and JAMES ERNEST MARSH.

The mercury compound $\text{HgC}_2\text{N}_{2.2}(\text{NH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_5)_3$ was found to act on a photographic plate even through a sheet of paper in a few hours, forming a deep black patch on development. When a perforated sheet of zinc was enclosed between two pieces of paper and interposed, the action was exerted through the perforations and the substance of the paper. The position occupied by the perforations was dense black; the rest of the film was only slightly affected owing to an action of the metallic zinc.

This mercury compound also acted strongly at some distance from the plate, even through a layer of aluminium foil. Through a disc of quartz, there appeared at the first attempt a just perceptible darkening, but on repeating the experiment the result was negative.

The substance was placed over strong sulphuric acid to test for loss due to evaporation; this proved to be extremely small.

The generators of the compound were tested separately: the action of phenylhydrazine was more sluggish and diffused than that of the compound; the behaviour of mercuric cyanide was less definite, some specimens being active, others inactive; the active specimens lost their activity after heating. Mercuric cyanide was distilled in a high vacuum without decomposition; the distillate was

inactive, even the most volatile portions. Inactive cyanide recovered its activity when slightly moistened with water; if covered with water, it was inactive.

Mercuric cyanide prepared from inactive mercuric oxide and hydrocyanic acid was active. Mercuric chloride was active, and retained its activity when distilled, both the distillate and residue being active. Mercuric bromide and mercuric and mercurous nitrates were active. Mercuric iodide, sulphate, acetate, sulphide, oxide, and mercuric ammonium chloride were inactive, or at the most very slightly active; as were also mercurous chloride, sulphate, acetate, and oxide. Re-distilled metallic mercury had no action whatever on a gelatin dry plate; cuprous silver and potassium cyanides were also inactive.

NOTICES OF BOOKS.

Alfred Cornu, 1841—1902. Rennes: Francis Simon. 1904.

THIS short biography of a gifted Frenchman gives an account of his most important work, which covered a wide range of subjects, almost all branches of physics having been enriched by some discovery made by him, and it will be found full of interest for physicists. The book contains two separate memoirs, both highly appreciative and sympathetic, but by no means redundant, since the subject of them is regarded in two different aspects. The first of these is by M. Poincaré, Membre de l'Institut, and deals with Cornu's work, and with his unique and striking talents, while the other, by L. de Lannay, is to be regarded more as a personal appreciation of a man of most estimable character. Both of these notices will be read with interest by the many scientific men of all nations who united in mourning the comparatively premature death of an investigator whose work was suddenly and unexpectedly interrupted, never to be resumed, in 1902.

Beiträge zur Chemischen Physiologie und Pathologie. ("Contributions to Chemical Physiology and Pathology"). Band VI., 5 Hft. Braunschweig: Friedrich Vieweg und Sohn. 1905.

THE January number of these *Beiträge* contains only four papers, which, however, are all of more than usual interest and importance. In the first, by Prof. H. Dreser, the author describes his researches on the intensity of the acidity of urine, upon which subject he has evidently done much careful work, without, however, obtaining any results of great significance. An article by Franz Steinitz and Richard Weigert, on the influence of a diet of carbohydrates upon the chemical composition of a suckling, describes investigations undertaken under somewhat singular conditions, from which conclusions may be drawn which are of fundamental importance from a dietetical point of view. The most interesting paper, however, is the last, by Richard Claus and Gustav Embden, on the pancreas and glycolysis. The authors have examined Cohnheim's statements regarding the joint glycolytic action of pancreatic juice and muscle juice, and have found that their experiments do not, on the whole, confirm these statements.

Über die Erddalkaliphosphore. ("The Phosphors of the Alkaline Earths"). By P. LENARD and V. KLATT. Leipzig: Johann Ambrosius Barth. 1904.

THESE reprints from the *Annalen der Physik* contain the accounts of the authors' exhaustive work on the phosphorescence of the sulphides of the alkaline earths. They have given the name "Phosphor" to such preparations as contain (1) the sulphide of an alkaline earth; (2) small traces of some active metal—copper, manganese, or bismuth; (3) some colourless fusible salt, such as sodium

sulphate or borate. They prepared some 800 such mixtures, and thoroughly investigated the intensity, colour, and duration of the phosphorescence, when changes are made in the third member of the phosphor, and also examined the influence of temperature upon the phosphorescence. The papers represent the result of an enormous amount of most thorough and careful work, and it is impossible even to touch upon the number of important points raised in them; allusion may, however, be made to the use of these phosphorescence phenomena in the detection of the most minute traces of certain metals, when all chemical methods and spark spectrum methods fail. This practical application of the peculiar phosphorescence, which may possibly lead to important results, is shortly discussed and illustrated.

CORRESPONDENCE.

LICENCE FOR LABORATORY STILLS.

To the Editor of the Chemical News.

SIR,—Some years ago the Revenue Inspectors exacted tribute from coal-gas manufacturers and others by compelling them to pay a licence for sulphate of ammonia stills! The matter was fought out by the Sulphate of Ammonia Association, and a stop was put to the exaction as a result of the cases Regina v. Illingworth and Regina v. The Sunderland Gas Company.

If this imposition is going to be revived, analysts as a body ought to oppose it. One way of doing it, whether the best I cannot say, would be for a representative body like the Institute of Chemistry to appoint a deputation to see the authorities on the matter. Even if G. F.'s be the only case it would be well for the matter to be promptly dealt with to prevent it becoming a habit with Revenue Inspectors.—I am, &c.,

WILLIAM ACKROYD.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

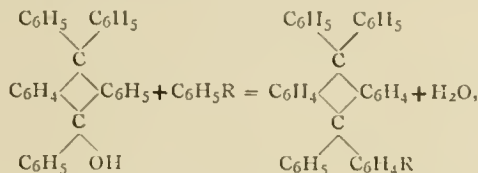
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxi., No. 5, January 30, 1905.

Tempering of Bronzes.—Léon Guillet.—The author finds that alloys containing more than 92 per cent of copper have their rupture charge slightly increased by tempering at a temperature between 400° and 600°. If the alloy contains less than 92 per cent of copper, the rupture and elongating stress increase in proportion as the tempering temperature exceeds 500°, the maximum being attained for a temperature of about 600°. The maximum of stretching appears, however, to alter with the composition of the alloy. With a metal containing Cu = 91 Sn = 9, the temperature being 800°, whilst it is only 600° for a metal of composition Cu = 79 Sn = 21. The difference between the rupture charge of the crude melted metal and that of metal tempered at the most favourable temperature is more accentuated as the proportion of copper decreases.

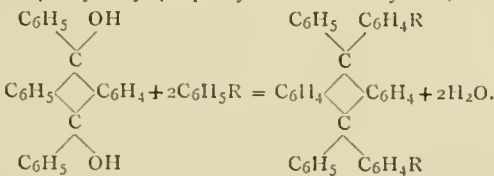
Colloidal Sesquioxide of Iron: Brown Modification.—P. Nicolardot.—Normal iron sesquioxide ought to be white, and, in fact, can be obtained in this state by pouring a concentrated and recently prepared ferric solution into cold liquid ammonia. However, in water or in absolute alcohol, iron sesquioxide precipitated from neutral or acid solutions is brown. This precipitated oxide has still further modifications, and it becomes little by little insoluble in

most acids. Ferric solutions themselves, as has been known for many years, become coloured by the action of time, heat, or dialysis. They become brown or red; they always contain either Graham's soluble oxide or Péan de Saint Gilles' soluble oxide. The author also obtains a yellow insoluble precipitate, which contains another modification of iron oxide, considered by all chemists as being an insoluble substance. He performs a series of experiments to explain these varieties, by showing that the molecule of iron sesquioxide can be obtained in different states of condensation.

Synthesis in the Anthracene Series. γ -Tetra-phenylanthracene Dihydride and its Derivatives.—M. Haller and A. Guyot.—The authors prepare the derivatives of γ -tetraphenyl anthracene dihydride, either by condensing the γ -hydroxyl- γ -triphenylanthracene dihydride (described in a previous paper) with aniline, phenol, dimethylaniline, &c., according to the equation—



or by condensing the same amines and phenol with symmetric γ -dihydroxyl- γ -diphenylanthracene dihydride,—



Chloruration of Methylene Ketone.—André Kling.—The author finds that the results obtained during an incomplete chloruration of methylene ketone do not differ much with the different chlorurating agents—Cl, Cl + I, SOCl₂, Cl + H₂O + CaCO₃. Nevertheless, with an aqueous solution of acetone, chlorine, and marble, the products are obtained in the purest form, and there are fewer tail products. The best conditions are fulfilled when 5 parts of ketone, 2.5 of water, and 1 of marble are mixed and chlorine rapidly passed through at a temperature of 70°. When all the marble is dissolved, the upper layer of liquid is decanted, dried over CaCl₂, the excess of ketone expelled, and the whole fractionated. The portion coming over between 114° and 117° is the chloro-ketone, CH₃CHClCOCH₃, which can be transformed by saponification into CH₃CHOHCOCH₃, and finally, by reduction, into the glycol CH₃CHOH.CHOH.CH₃.

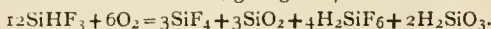
Action of Dilute Nitric Acid on Vegetable Fibres.—M. Jardin.—The author's experiments on dyeing of vegetable fibres show that oxygen compounds of nitrogen, and especially dilute nitric acid, are capable of inducing slow oxidation of vegetable fibres. This action has various commercial advantages, e.g., economy of time and manual labour, besides perfect homogeneity of the fibre, which latter, therefore, lends itself to a regular impregnation of the dye.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxviii., No. 1, 1905.

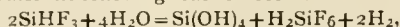
Action of Silico-chloroform on Fluorides, and the Preparation and Properties of Silico-fluoroform.—Otto Ruff and Curt Albert.—On gently heating a mixture of antimony trifluoride and silico-chloroform in a closed tube the mass turns black, gas is evolved, and the following reaction takes place:—



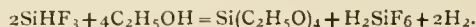
A violent reaction occurs at the ordinary temperature when arsenic trifluoride and silico-chloroform are brought together. On examining the reaction quantitatively it was found that it did not proceed as represented by the above equation, and it seemed likely that some silico-fluoroform was produced. Tin tetrafluoride and silico-chloroform on being heated to about 220° for a day in a closed tube yield a homogeneous liquid. On opening the tube under liquid air the escaping gas (silico-fluoroform) may be collected. The reaction appears to proceed according to the equation $3\text{SnF}_4 + 4\text{SiHCl}_3 = 4\text{SiHF}_3 + 3\text{SnCl}_4$. When the gas is brought into contact with caustic soda over mercury hydrogen is very energetically evolved, but no alteration occurs in the total volume of gas. With titanium tetrafluoride the reaction occurs at 100°, and this was found to be the most convenient method of preparing the gas in large quantity, *i.e.*, heating the molecular quantities of titanium tetrafluoride and silico-chloroform in a copper bulb in an oil-bath for eighteen hours at a temperature of 100° to 120°. The bulb was cooled in liquid air, and the gas was condensed in liquid air; the residue in the bulb consisted of excess of titanium tetrafluoride and titanium tetrachloride. The boiling-point of silico-fluoroform is -80.2° at 758.5 m.m. pressure (corr.); sublimation-point, -90° at 759.0 m.m. (corr.); melting-point, -110° (about). When heated in a closed tube it deposits some brown silicon at 420°, and after a time a glittering mirror is obtained. The compound decomposes according to the equation $4\text{SiHF}_3 = 2\text{H}_2 + 3\text{SiF}_4 + \text{Si}$. It burns in air with an almost colourless flame, giving SiF_4 :—



With water the following reaction occurs :—



and with alcohol—



Condensation of Benzaldehyde with Toluene.—A. Kliegl.—Benzaldehyde in presence of concentrated sulphuric acid does not act upon benzene, but if a mixture of benzaldehyde, toluene, and concentrated sulphuric acid is shaken for three or four days a slow condensation takes place, which is clearly due to the "wandering" of the *p*-hydrogen atom in the toluene. After driving off the excess of the reagents by means of a current of hydrogen and purifying the raw product with ether, a colourless syrup is obtained from which crystals separate out. These consist of the hydrocarbon, $\text{C}_{21}\text{H}_{20}$, which is identical with the product obtained by the reduction (with zinc dust and acetic acid) of di-*p*-tolyl-phenyl-carbinol, prepared synthetically from benzoic acid ester and *p*-bromotoluol.

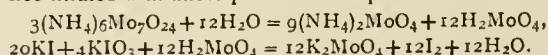
Weber's Dinitro-caoutchouc.—C. Harries.—Weber has described the preparation of a dinitro compound (nitrosate) of caoutchouc, and recommends its use for the quantitative determination of the latter. The author cannot obtain this product, but by the action of hyponitrous acid on caoutchouc he gets a substance which has the properties and approximately the composition of the soluble nitrosite, $(\text{C}_{10}\text{H}_{15}\text{N}_3\text{O}_7)_2$. In investigating the action of nitrogen dioxide on caoutchouc he finds that the length of time during which the nitrogen dioxide is in contact with the substance which separates from para-caoutchouc has an important effect upon the product obtained. Thus, if the precipitate, formed by the action of NO_2 on para-caoutchouc, is filtered off at once it is found to have quite different properties from those ascribed to it by Weber. But if it is allowed to stand for an hour at the ordinary temperature, it then appears to possess all the properties of Weber's compound, but not its composition. It seems probable that the continued treatment of caoutchouc with NO_2 would yield the same products as those obtained with the so-called raw nitrous acid, but it is much more difficult to obtain constant products with the former than with the latter.

Pentasulphides of Rubidium and Cæsium.—Wilhelm Biltz and Ernst Wilke-Dörfurt.—To prepare the

pentasulphides of rubidium and cæsium a solution of sulphhydrate (made by saturating a solution of the hydroxide with H_2S) was added to finely powdered sulphur and N=2N alkali in a flask, the air in which had been replaced by an atmosphere of hydrogen. The mixture rapidly turns yellow in the cold, becoming darker when cautiously warmed, till at last the liquid is opaque. It is then concentrated till it attains the consistency of concentrated sulphuric acid, and then after ten to twenty hours dark red crystals separate out, which may be dried *in vacuo* over CaCl_2 . Rubidium pentasulphide deliquesces in the air to a dark red liquid from which sulphur soon crystallises. It melts at 223–224°. Specific gravity, 2.618 (at 15°). It is very easily soluble in 70 per cent alcohol. Cæsium pentasulphide is more stable in air than the rubidium compound, and is not hygroscopic, remaining unchanged in air for two days. After four days it becomes covered superficially with microscopic white needles, which do not penetrate into the interior even after seven days. It dissolves in the cold in 70 per cent alcohol to a dark red liquid from which red crystals separate, no sulphur being deposited. The melting-point lies between 202° and 205°.

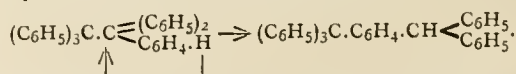
Use of Microbalance for Analyses.—O. Brill.—Nernst's microbalance, as supplied by the firm of Spindler and Hoyer, of Göttingen, is sensitive to about 0.001 m.grm., and gives very accurate results, being specially suitable for use (1) when accurate analyses have to be performed with the smallest possible quantity of substance, as, for example, in the determination of the constitution of organic compounds; (2) in cases in which rapidity is essential; (3) when working with hygroscopic substances or with those which readily suffer change in the air; (4) when it is necessary to maintain constant temperatures, when the electrical oven will be found very useful. Before using the balance the constancy of the zero point should be carefully examined. Sealing-wax or celluloid cement should be used rather than water-glass for all cementing in the balance. The sensitiveness is perfectly constant only between comparatively small limits, *e.g.*, 80–100 scale divisions. The base of the balance-case should preferably be composed of glass or slate, and it should never be placed upon wood. The pointer should be at a distance of 2 or 3 m.m. from the scale.

New Iodometric Method of Determining the Alkali Heptamolybdates.—B. Glassmann.—A mixture of 0.2–0.3 gm. of a heptamolybdate, 0.5 gm. of potassium iodide, and 0.1 gm. of potassium iodate is boiled with distilled water in Bunsen's apparatus; the distillate in the flask is added to the liquid in the retort, and the iodine set free titrated with thiosulphate. The equations are—



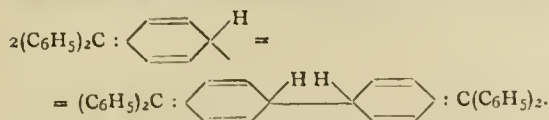
Thus 0.822 part by weight of iodine correspond to 1 of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} + 4\text{H}_2\text{O}$. This method is found to be very accurate in practice.

The Triphenyl-methyl Question.—P. Jacobson.—The author regards Tschitschibabin's experiments as quite convincing with reference to Ullmann and Borsum's "hexaphenyl ethane," but cannot accept his conclusions regarding the constitution of Gomberg's "triphenyl-methyl," particularly as he makes no mention of the fact that the latter very readily yields hexaphenylethane on treatment with hydrochloric acid. This would have to be due to a very deep-seated molecular transformation, thus—



which, though not without precedent, cannot be regarded as probable. But if we accept Gomberg's formula for triphenyl-methyl and Tschitschibabin's for hexaphenylethane, the change would be represented by a simple polymerisation. The author now suggests a new formula,

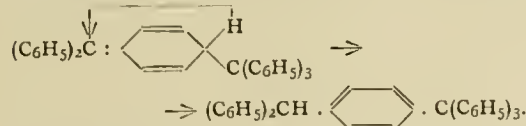
which seems to solve the mystery of triphenyl-methyl. Heintschel suggested two quinoid residues united thus:—



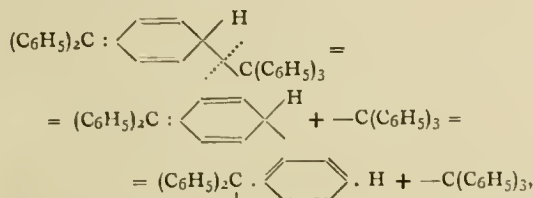
If now we take a quinoid triphenyl-methyl residue united with a non-quinoid we seem to arrive at a suitable formula, viz. :—



The formation of Ullmann and Borsum's hydrocarbon would then occur thus:—

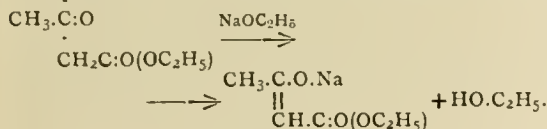


Thus Gomberg's hydrocarbon would be merely the quinoid form of Ullmann and Borsum's. But if the triphenyl-methyl residue were released as shown in the following equations, one quinoid triphenyl-methyl residue would remain, and by an alteration of linkage could pass into an aromatic triphenyl-methyl residue,—

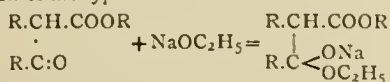


i.e., such a substance could behave like free triphenyl-methyl. This new formula would also explain Gomberg's molecular weight determinations.

Sodium Aceto-acetic Ester.—J. W. Brühl and H. Schröder.—On determining the molecular dispersion of this salt in solution and in the homogeneous state, it was found that the dispersion in the case of the dissolved ester in all degrees of concentration is almost three times as great as that of the homogeneous substance. From this it appears that on the formation of the salt aceto-acetic ester is totally altered—enolised. The change in formation takes place thus:—



It may readily be proved that the optical increments are not due merely to the union of a metal with a COO radicle, but are actually caused by enolisation, for the optical phenomena occur when tautomeric transpositions of keto-enol desmotropic substances take place in neutral solution, when no salt can be formed. From the fact that a condensation of the type—



would involve the replacing of a double bond, C:O, by single bonds, and thus would lead to a decrease, and not an increase of the optical function, it may be deduced

that the reaction of sodium aceto-acetic ester in alcoholic solution is not additive but substitutive, thus:—
 $C_6H_{10}O_3 + C_2H_5 \cdot ONa = C_6H_9NaO_3 + C_2H_5 \cdot OH$, a transposition product of enol nature being formed.

Molecular Weight Determinations by Rise in Boiling Point in the Vacuum of the Cathode Light.—F. Kraft and Paul Lehmann.—The authors have already shown that the boiling point of substances of high molecular weight in the vacuum of the cathode light is a function of the molecular weight, and also of the height of the column of vapour produced. They have now investigated a large number of substances, and find that if M is the molecular weight, E the difference in temperature between the widest removed layers of vapour of the substance boiling *in vacuo*, as registered by the upper and lower thermometers, and C a constant of the apparatus determined by means of a known substance, then $M = E \times C$.

MISCELLANEOUS.

The Cold Storage and Ice Association.—At the next meeting of the Cold Storage and Ice Association, which will be held at the Caxton Hall, Caxton Street, Westminster (near St. James's Park District Railway Station), on Tuesday, March 7th, at 7.30 p.m., Mr. Charles Page will read a paper on "The Production of Ammonia." The paper will be illustrated with lantern views, and followed by discussion. Application for tickets of admission should be made to the Honorary Secretary, at 19, Ludgate Hill, London, E.C.

MEETINGS FOR THE WEEK.

- MONDAY, 6th.—Society of Arts, 8. (Cantor Lecture). "Internal Combustion Engines," by D. Clerk, M.Inst.C.E.
— Society of Chemical Industry, 8. "Mechanics of Fire," by Prof. H. E. Armstrong. "Estimation of Arsenic in Fuels—a Shortened Method," by G. McGowan and R. R. Floris.
— Royal Institution, 5. General Monthly Meeting.
TUESDAY, 7th.—Royal Institution, 5. "Some Recent Biometric Studies," by Prof. Karl Pearson, F.R.S.
WEDNESDAY, 8th.—Society of Arts, 8. "Ethics of Japanese Society," Baron Suyematsu.
THURSDAY, 9th.—Royal Institution, 5. "Recent Astronomical Progress," by Prof. H. H. Turner, F.R.S.
FRIDAY, 10th.—Royal Institution, 9. "Structure of the Atom," by Prof. J. J. Thomson, F.R.S., &c.
— Physical, 8. "Stresses in the Earth's Crust before and after the Sinking of a Bore-hole," by Dr. C. Chree. "Lateral Vibration of Bars of Uniform and Varying Sectional Area," by J. Morrow. "Direct-reading Resistance Thermometers, with an Appendix on Composite Thermocouples," by A. Campbell.
SATURDAY, 11th.—Royal Institution, 3. "Electrical Properties of Radio-active Substances," by Prof. J. J. Thomson, F.R.S., &c.

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THE CHEMICAL NEWS.

VOL. XCI., No. 2363.

ON EUROPIUM AND ITS ULTRA-VIOLET SPECTRUM.*

By Sir WILLIAM CROOKES, D.Sc., F.R.S.

EUROPIUM was discovered in 1901 by Demarçay (*Comptes Rendus*, vol. cxxxii., p. 1484, and *CHEMICAL NEWS*, vol. lxxv., p. 1), accompanying samarium, from which he separated it by fractional crystallisation of the double nitrates of magnesium and the earths. Demarçay considered that his new earth was identical with De Boisbaudran's Z_4 and Z_5 , and was the same which I had announced in 1885 (*Phil. Trans.*, vol. clxxvi., p. 691) as giving an extremely sharp red line in the phosphorescent spectrum at wave-length 609—an earth which in 1889 (*Journ. Chem. Soc.*, vol. lv., pp. 250—285) I said was a new one, and designated by the name of S_2 .

I detected the earth S_2 during an examination of the phosphorescent spectra given by some of the fractions of samaria and of yttria, neither of the earths being pure.

Europium is the first member of the terbium group, gadolinium being the second member. On the other side it comes next to samarium, the last member of the cerium group.

Assuming the oxide of europium to be Eu_2O_3 , the element has an atomic weight of 151.8, from the analysis of its sulphate, $\text{Eu}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$.

MM. Urbain and Lacombe (*Comptes Rendus*, vol. cxxxviii., pp. 84, 627, 1166; *CHEMICAL NEWS*, vol. lxxxix., pp. 52, 179, 277) have sharply separated europium from samarium in the manner outlined by them in my note on gadolinium (*Roy. Soc. Proc.*, vol. lxxiv., p. 420) by fractional crystallisation of the double nitrates of bismuth or magnesium with the nitrates of the rare earths. I owe to the kindness of M. Urbain a sufficient quantity of the oxide of europium to enable me to obtain a good series of its photographed spectrum, a copy of which accompanies the present paper.

Exner and Haschek have measured the wave-lengths of the europium lines ("Wellenlängen-Tabellen für Spektralanalytische Untersuchungen," F. Deuticke, Leipzig und Wien, 1902) from material supplied by Demarçay. A comparison of their lines with mine shows that the material was by no means pure.

Urbain's europia is not quite so free from impurities as his gadolinia. I have been able to detect in my photographs the following lines:—Gadolinium is represented by very faint lines at 3450.55, 3481.99, 3585.10, 3646.36, 3654.79, 3656.32, 3664.76, 3697.90, 3699.89, 3743.62, 3768.52, 3796.58, 3805.70, 3850.83, 3851.16, 4050.08, 4225.33. Yttrium is represented by the line at 3774.51, lanthanum by the line at 3988.66, and calcium by the two lines at 3933.825 and 3968.625.

No lines of bismuth or magnesium are to be seen.

Most of the lines of impurities are exceedingly faint, showing that the impurity is only present in very minute proportion. Indeed, I have only mentioned them if they correspond with strong lines in the gadolinium or other spectrum.

Both in the europium and the gadolinium spectrum I have not attempted to give wave-lengths of all the excessively faint lines. If at some future time it becomes of interest or value to ascertain their wave-lengths, all the necessary data are present whereby they can be identified.

EXAMINATION OF THE CARBON SILICIDE IN THE CAÑON DIABLO METEORITE.

By HENRI MOISSAN.

CONTINUING my investigations on the Cañon Diablo meteorite, I came across crystals whose form was identical with that of carbon silicide of formula SiC . On examining the residue left from a block of 53 kilos., which had been dissolved in hydrochloric acid, it was possible to isolate a very small quantity of this compound and to determine its exact nature.

This substance extracted from the Cañon Diablo meteorite is sometimes found in the form of hexagonal crystals, with very pointed ends and perpendicular sides, and sometimes in the form of broken fragments always showing angles which belong to the hexagonal form. The different pieces are all coloured mostly of a more or less dark green, sometimes a bright emerald green, like the crystals of carbon silicide obtained in ferro-nickel.

Bromoform of density 2.9 mixes in all proportions with pure methylene iodide of density 3.4. The crystals obtained in the above manner sink in bromoform and float on methylene iodide. By mixing these two substances two liquids can be obtained of respective densities 3 and 3.2. The crystals float on the latter and sink in the former. Their density is therefore intermediate between these two values. It corresponds very satisfactorily with the density of carbon silicide, which I previously determined to be 3.2.

I further performed several chemical reactions on small fragments extracted from the meteorite. The substance does not burn in oxygen at 1000°. It is not attacked by potassium chlorate or nitrate in a state of fusion.

Sulphuric, nitric, and concentrated hydrochloric acids do not decompose it at their boiling points. It is also unattacked by aqua regia, a mixture of nitric and hydrofluoric acids, and a mixture of nitric acid and potassium chlorate. Fusing caustic potash disintegrates it slowly with formation of potassium silicate, which can be easily identified. Lead chromate also attacks it when in a state of fusion, giving off carbon di-oxide.

The conclusion to be drawn from the results of these reactions is that carbon silicide does exist in the Cañon Diablo meteorite. Whether this block of iron is of terrestrial or sidereal origin, the existence of carbon silicide amongst the metal itself shows that products only prepared at the temperature of the electric furnace are present in nature.—*Comptes Rendus*, vol. cxl., No. 7, p. 193.

The Causes which Accelerate or Retard the Auto-inversion of Saccharose.—L. Lindet. —The author finds that the conductivity of water being 1, that of saccharose, through its slight acidity, is 1.3, that of levulose 3.7, and that of glucose 5.1. He also finds that the addition of 1/3000th part of invert sugar causes a change from the simple to the double autoinversion of saccharose, and that various refined commercial sugars give larger quantities of reducing sugars, as the sugar contains more glucose. If the inversion is effected in a glass vessel, the liquid dissolves a quantity of alkaline silicates sufficient to saturate the slight acidity of the sugar, and thus retard or stop altogether the formation of reducing sugars. Results of a more variable character are obtained by using vessels made of zinc, aluminium, lead, tin, copper, &c. As a matter of fact, copper, lead, tin, and bismuth accelerate the inversion considerably; aluminium and antimony do so slightly; nickel, chromium, gold, platinum, arsenic, silver, and mercury have no action; while cobalt, cadmium, manganese, iron, zinc, and magnesium retard it. The author then proceeds to discuss the causes of these different actions.—*Bull. Soc. Chim.*, Series 3, xxxi., No. 8.

* A Paper read before the Royal Society, February 9, 1905.

ON A METHOD IN QUALITATIVE
ANALYSIS FOR DETERMINING THE PRESENCE
OF CERTAIN METALLIC OXIDES.

By CHAS. R. C. TICHBORNE, F.I.C. Dip. P.H.L. I.C.S., &c.

THE determination of the presence of an oxide either in a mixture or by itself is not always easy; in fact, it is largely indicated by the negation of special reactions, and by the analyst's knowledge of the special properties of the well-known oxides.

A recent text-book by an authority on analysis speaks of this question in the following manner (Atfield's "Chemistry," 17th edition, p. 453) :—

"If no acidulous radical can be detected in a substance under analytic examination, or if the amount found is obviously insufficient to saturate the quantity of basylous radical present, the occurrence of oxides or hydroxides, or both, may be suspected. . . . Hydroxides and oxides insoluble in water not only neutralise much nitric acid, or acetic acid, but are thereby converted into salts soluble in water. Most oxides and hydroxides have a characteristic appearance. In short, some one or more properties of an oxide or hydroxide will generally betray its presence to the student who not only has knowledge respecting chemical substances, but has cultivated the faculties of observation and perception."

If the above quotation fairly represents the method now in use, it is certainly not very definite.

To the experienced analyst the ordinary reactions of well-known oxides rarely present a difficulty; but it is not so with most students, who, lacking a general experience, are often sorely puzzled how to make up their minds on such questions.

Under these circumstances an easily applied test of a general character is desirable.

The test I propose is based upon a very simple reaction between the indicator, phenolphthalein, and the carbonates of sodium. This indicator, phenolphthalein, as is well known, whilst colourless in neutral solutions, is crimson in solutions of alkalis and alkaline carbonates, but it is also colourless in solutions of acid-carbonates.

The test solution I use is made by dissolving 10 per cent of pure sodium acid-carbonate in distilled water. If this solution is tested with phenolphthalein, it will probably give a faint pinkish colouration, although the sodium acid-carbonate may be perfectly pure. The act of dissolving it produces a slight dissociation. This colouration is indeed so slight that in practice it might be ignored. I prefer, however, to gradually add a few drops of a normal solution of nitric acid. After this treatment we get a solution which is quite colourless when tested with phenolphthalein. If the sodium acid-carbonate solution has been laid by for some time, it must be again brought to the neutral stage.

List of the Oxides Examined as regards their Reaction with Sodium Acid Carbonate and Phenolphthalein.

Name.	Variety.	Observations.
Lead, PbO	Litharge	Gives the reaction very readily.
Lead, Pb ₃ O ₄	Minium, or red-lead	No reaction.
Silver, Ag ₂ O	Pharmacopœia	Gives the reaction readily.
Mercury, Hg ₂ O	Precipitated oxide, well washed	No reaction.
Mercury, HgO	Yellow, precipitated	Marked reaction best obtained by trituration process.
Mercury, HgO	Red crystalline	Reactions obtained, but in a less marked manner than with the yellow variety; test-tube process.
Copper, Cu ₂ O	Cuprous oxide by reduction	Gives the reaction badly. The most satisfactory results obtained by digesting for some time in the test-tube.
Copper, CuO	By precipitation and ignition of carbonate	No effect.
Bismuth, Bi ₂ O ₃	Pharmacopœia	Marked reaction by the trituration process.
Tin, SnO ₂	Putty powder	Marked reaction by either process.
Antimony, Sb ₄ O ₆	Pharmacopœia	Marked reaction by trituration process.
Aluminium, Al ₂ O ₃	—	No reaction.
Iron, FeO	Moist	Marked reaction by trituration process.
Iron, Fe ₃ O ₄	Magnetic oxide by precipitation	Marked reaction by trituration process.
Iron, Fe ₂ O ₃	By precipitation	No reaction.
Manganese, MnO	By precipitation	Marked reaction by trituration process.
Manganese, MnO ₂	—	No reaction.
Zinc, ZnO	Flowers of zinc	Well-marked reaction.
—	Oxide by ignition of the carbonate	Well-marked reaction by trituration process.

Most metallic oxides, acting on this solution, will reduce a normal proportion of the acid carbonate to the normal carbonate, according to the following equation:—
 $\text{MO} + 2\text{NaHCO}_3 = \text{Na}_2\text{CO}_3 + \text{MCO}_3 + \text{H}_2\text{O}.$

I find that most of the hydroxides, and oxides formed in the moist way, will bring about this decomposition. Those that have been ignited do not, as a rule, act so well.

The test may be applied in two ways:—

1. A little of the suspected substance is rubbed in a mortar with 2 or 3 c.c. of the sodium acid-carbonate solution. It is then thrown upon a filter; and if it contains any of the specified oxides, the filtrate will immediately give a deep crimson colouration with the phenol-phthalein solution. The object of rubbing in a mortar is, that as we are dealing with insoluble oxides and insoluble carbonates, the reaction is rather slow unless this device is adopted.
2. If time is no object, it is not necessary to do this. The suspected substance is shaken occasionally for about an hour in a test-tube, when the decomposition will be sufficiently advanced to give a marked reaction. On testing the filtrate from such an experiment, heat should not be applied. Dissociation of carbonic acid takes place, resulting in permanent decomposition when operating in an open tube.

The oxides of the alkaline earths and the alkalis give the reaction; but, of course, their own alkaline reaction is sufficiently marked to render an experiment with the sodium acid-carbonate superfluous.

Magnesium carbonate, $3\text{MgCO}_3 \cdot \text{Mg}(\text{HO})_2 \cdot 4\text{H}_2\text{O}$, and bismuth carbonate, $2(\text{Bi}_2\text{O}_3 \cdot \text{CO}_3) \cdot \text{H}_2\text{O}$, being basic carbonates, give a slight pink tinge, but present no diagnostic difficulty, owing to the evolution of CO_2 on acidulation.

The ferric oxide and alumina, as might naturally be expected, give no reactions, as the carbonates are not known to exist. We thus see that this reaction is of very general application; but it is right that we should bear in mind that some of the ignited oxides lose more or less the power of decomposing the acid carbonate. The same remark applies to most of the mineral oxides as found in nature.—*Scientific Proceedings of the Royal Dublin Society*, x., Part II., No. 28.

THE ACTION OF CYANIDE OF POTASSIUM ON METALLIC ELECTRODES.

By ANDRÉ BROCHET and JOSEPH PETIT.

THE electrolysis of the solution of cyanide of potassium, while using different metals as electrodes, was of the highest importance during our research on electrolysis by means of an alternating current.

The present series of experiments was carried out while using a solution of cyanide at 4 grm.-molecules per litre.

Though most of the metals dissolve at the anode, others act as insoluble anodes, or at least we may look upon them as such; for instance, iron (*Bull. Soc. Chim.*, Series 3, vol. xxvi., p. 740) and platinum, of which the consumption is very small. But under these conditions the amount of oxygen given off is according to circumstances nil or insignificant with regard to the oxidation of the cyanide.

With platinum the liquid becomes black, and a dark coloured deposit is formed on the anode. The electrolyte remains colourless, as we have remarked already, if we add an excess of potash. With an anode of iron there is no black colouration.

A large number of metals, copper, zinc, cadmium, silver . . . dissolve quantitatively when they are used as anodes and within fairly wide limits of density of current.

Nickel dissolves quantitatively with a feeble current (less than 2 ampères per square decimetre). With 6 ampères per square decimetre the solution of the metal is not more

than 90 per cent of theory; if the density of the current increases the amount of metal going into solution diminishes, and tends towards a limit of 80 per cent. This fact was observed by Le Blanc and Schick (*Zeit. Physik. Chem.*, vol. xlvii., p. 633) amongst others, but they obtained slightly different results.

Cobalt is always dissolved with a low return, and the strip is badly pitted; the attack takes place at points, which makes any observation of the density of the current quite superfluous. The same occurs with nickel when the solution is not according to theory.

Mercury is dissolved when it is used as an anode, but it is rapidly covered with a black precipitate which stops the current. Amalgamated copper and zinc dissolve quantitatively. Lead has only an insignificant action.

Let us now consider the deposit of metals on the cathode by simply taking the case in which the metal in solution is furnished entirely by the anode.

Silver commences to be deposited as soon as there is a very small quantity in solution. The ratio between the metal deposited on the cathode and the metal dissolved at the anode increases rapidly, in spite of the large excess of cyanide.

Cadmium behaves in an identical manner, but less distinctly. With zinc, copper, and nickel the deposition is very difficult as long as free cyanide remains in solution. With cobalt and iron the deposition is practically impossible.

From another point of view, by using an insoluble anode, and a suitable dilution and density of current, we know that we can estimate silver, cadmium, zinc, copper, and even nickel by the intermediary of double cyanides.

Platinum, as we have stated above, behaves as an insoluble anode. The attack is insignificant; however, we have found that it is not negligible.

Glaser (*Zeit. Elektroch.*, vol. ix., p. 11) and Ruer (*Zeit. Phys. Chem.*, vol. xlv., p. 81) have established the fact that under certain conditions the platinum used as the cathode is dissolved in the presence of cyanide of potassium. At any rate, the amount of solution observed by these two chemists was about 0.001 grm.; we therefore decided to confirm this observation by an experiment of long duration.

We took two strips, which had been used for various electrolyses, having a surface of 32 sq. centims., and we used them as the electrodes in an apparatus containing 450 c.c. of solution of cyanide, and passed a current of 2 ampères, that is to say, 6 ampères per square decimetre, for forty-eight hours. The liquid commenced by turning black; after twenty-four hours a distinct evolution of gas was observed at the anode. During the experiment the temperature was maintained at 45–50°; at the end of the experiment the anode had lost 0.001 grm. and the cathode 0.081 grm.

We re-commenced the experiment with a fresh solution; after six hours the loss of the cathode was 0.030 grm. By changing the direction of the current so as to make the cathode the anode, and *vice versa*, we observed a loss of 0.35 grm. after fifteen hours, this diminution of attack being due to the impoverishment of the solution of cyanide. In these last experiments the anode did not lose weight to any appreciable extent.

We may remark here that this attack, which is important with regard to the value of the metal, is entirely negligible if considered from the point of view of the chemical action itself.

Following up our experiments, we observed that the attack on the cathode is much greater in the presence of cyanide of barium. A cathode of 5 sq. centims., submitted to the action of a current of 3 ampères for fifteen minutes, lost 0.001 grm. in cyanide of potassium, while with cyanide of barium the loss of weight observed in five different experiments varied from 0.056 grm. to 0.177 grm. Here we have to do with an important case of solution of an entirely different order to that observed in the case of cyanide of potassium.

How does this solution of the platinum at the cathode take place?

Naturally, we cannot admit that it takes place in the same manner as the usual solution of an anode. The most reasonable hypothesis is that of the disaggregation of the cathode followed by the spontaneous solution of the platinum.

The phenomenon of the mechanical destruction of cathodes has already been observed many times. Bredig and Haber (*Ber.*, vol. xxxi., p. 27), Haber and Sack (*Zeit. f. Elektroch.*, vol. viii., p. 245) have shown that cathodes of lead and tin in the presence of alkaline salts are transformed into powder in the liquid; they are of the opinion that this fact is due to the transitory formation of an alloy with the alkaline metal. The difficulty of making an alloy with hydrogen will explain why pulverisation is not easily effected in acid solutions.

From another point of view, Bredig (*Zeit. f. Angew. Chem.*, 1898, p. 951), regarding the fact that the cathode in vacuum tubes are pulverised, passed a spark between two metal poles placed under water.

In this manner he obtained the pulverisation of the cathode with the formation of colloidal metals, platinum, silver, &c.

The silver thus obtained dissolves instantly in cold cyanide of potassium, while the platinum dissolves very slowly at boiling temperature; however, a certain quantity goes into solution at the ordinary temperature.

By analogy with what has been stated above, the pulverisation of the platinum cathodes should take place more easily in an alkaline medium than in an acid one, and the electrode becomes covered with a black film. The phenomenon was observed by Haber (*Zeit. Anorg. Chem.*, vol. xvi., p. 147). We may remark that Bran (*Zeit. f. Elektroch.*, vol. viii., p. 197) pointed out the solution of platinum at the cathode in the electrolysis of hydrochloric acid. He noticed the mechanical destruction followed by the solution of the metal, thanks to the chlorine in solution.

The presence in the alkaline electrolyte of a solvent of platinum naturally favours this mechanical pulverisation by removing the platinum-black as it is formed, more or less rapidly. This explains the action of the cyanides of potassium and barium. The particles of platinum torn from the cathode appear to be more attenuated than those of the colloidal platinum of Bredig, since they dissolve almost instantly, even in contact with the electrode.

However, in all the above-mentioned experiments, and particularly in those carried out in the presence of cyanide of barium, we have observed, after the cessation of the current, a disengagement of gas, either in the body of the liquid itself, or from the deposit, if there is one. This arises from the spontaneous solution in the cyanide of invisible particles of platinum detached from the cathode. The gas collected is hydrogen, and it keeps coming off for an hour or two, and sometimes for even a longer period.

We are not able at present to explain why the destruction of the cathode under the influence of cyanide of barium is more considerable than in the presence of cyanide of potassium. Perhaps the alloy, of which we presume the transitory existence, is formed more easily with barium than with potassium; perhaps in the former case the resulting platinum is more finely divided and therefore more easily soluble.

As for the non-concordant results we found, with regard to the cathodic solution in cyanide of barium, they are more easy to interpret.

The mechanical disaggregation may be influenced by many causes; the history of the electrode especially is of great importance. In the series of experiments quoted above, that one corresponding to the loss of 0.079 gm. was made with a cathode that had already been used for the electrolysis of cyanide of potassium. This experiment was followed immediately by another under the same conditions, and which gave us a loss of 0.101 gm. An experiment made with an electrode, previously used for the electrolysis of a solution of hydrate of baryta with an

alternating current, gave us a loss of 0.177 gm. When repeated immediately it gave a loss of only 0.130 gm. Thus it does not seem possible to fit in these phenomena with any general law, their importance depends on the physical condition of the metal used, and more especially on the condition of its surface.—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 23.

ON SOME CUPRAMMONIUM SULPHATES.*

By DAVID W. HORN and EDYTHA E. TAYLOR.

(Concluded from p. 101).

V. Properties of Aqueous Solutions of the Salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$.

1. ALL solutions of the salt have quite a strong odour of ammonia. The tension of ammonia over a solution of copper sulphate to which an excess of ammonia has been added is less than over an aqueous solution of ammonia of the same concentration. If the tension in a given case be corrected by subtracting from the total tension that due to 4 gm.-molecules of ammonia for every gm.-atom of copper present, the corrected tension is less than that actually observed. Locke and Forssell have recently interpreted this excess of tension as due to the lesser solubility of ammonia in cuprammonium sulphate solutions than in water (*Am. Chem. Journ.*, 1904, xxxi., 268). They assume that the complex cuprammonium salt and the complex cuprammonium ion do not affect the tension at all by their dissociation.

It is true that if the salt underwent any considerable molecular dissociation with loss of ammonia, we could not have kept it in a bell-jar over lime for more than a year without decomposition (see p. 78), and it would lose weight in a vacuum over sulphuric acid much faster than we found that it did (see p. 78). On the other hand, the facts that the salt smells strongly of ammonia at once when moistened, that the decomposition by water is so rapid that the salt cannot be dried between filter papers, and that all of its solutions smell strongly of ammonia, are not in accord with their assumption. There is sufficient reason in these facts to believe that the excess tension of ammonia is due at least in part to the hydrolytic dissociation with loss of ammonia of the complex salt or its electrolytic dissociation-products.

2. The salt gives a clear solution when water is poured gradually upon it; but, if the addition of water is continued, a permanent precipitate is formed at about N 20 to N 25 concentration. (These concentrations are fractions of "molecular normal"). When a solution of the salt is dropped into water a permanent precipitate is formed at once.

3. A N 10 solution of the salt, after standing a couple of days in a tightly-closed vessel, begins to deposit a crystalline blue solid; this continues for weeks.

4. If a current of air (free from carbon dioxide) is passed through a N/10 solution of the salt, ammonia is removed by the air, and after about twenty-four hours a finely crystalline blue deposit begins to form on the walls of the vessel. This precipitate increases in bulk throughout a long period of time.

5. When a solution of the pure salt—or of the pure salt with an excess of ammonia—is titrated into acids, the precipitate at first formed re-dissolves until a definite limit is reached, when the precipitate becomes permanent. This point at which the precipitate becomes permanent is very sharp, and, in a solution of the pure salt, lies very close to the point of neutrality of the liquid. This point is also independent of the anion of the acid used, at least in the case of strong acids. The following figures present a comparison of the weights of different acids used up by 1 c.c. of a given salt solution with the weights of the same acids

* From the *American Chemical Journal*, xxxii., No. 3.

calculated as just equivalent to the ammonia of the salt in 1 c.c. of the given solution. They also show that the nature of the anion of the acid is without effect:—

	Calculated. Grm.	Found. Grm.
HCl	0.0147	0.0146
H ₂ SO ₄	0.0198	0.0192
HNO ₃	0.0255	0.0252

6. Pure copper sulphate is very approximately neutral to methyl-orange indicator. This indicator can be used to determine the alkalinity of the liquids in which the permanent precipitate described in 5 is formed. The following results show the definiteness of the methyl-orange end-reaction under these conditions, as well as that of the reaction indicated by the permanent precipitate. They also show that the precipitate forms in a feebly alkaline solution:—

Volume of acid required by 1 c.c. cuprammonium solution to give permanent precipitate.	Volume of acid required by same to give neutrality to methyl-orange.
C.c.	C.c.
1.93	1.98
1.94	1.98
1.94	1.98
2.32	2.38
2.32	2.38
2.33	2.38
3.03	3.12
3.04	3.11
3.04	3.11

7. The reaction indicated by the permanent precipitate is affected by the presence of ammonia, as is also the neutralisation indicated by methyl-orange. In neither case is the effect proportional to the ammonia added. The following results set forth these points:—

Number of solution.	Molecular concentration of solution with respect to copper.	Ratio Cu : NH ₃ in solution.	Ratio Cu : H at time of permanent precipitation.	Ratio Cu : H at time of neutrality to methyl-orange.
I.	N 9.87	1 : 4	1 : 3.88	1 : 3.97
II.	N 9.95	1 : 4.82	1 : 4.65	1 : 4.77
III.	N 9.55	1 : 6.06	1 : 5.84	1 : 5.99

8. In a given solution both of these reactions change with time. The total alkalinity diminishes, and the alkalinity at the moment when the permanent precipitate is formed increases. The presence of an excess of ammonia does not prevent this displacement of the two end-reactions with time. Thus, after Solution I., above, had deposited some of the blue solid mentioned in 3, the alkalinity at the moment of permanent precipitation had

increased from 0.09 to 0.12 grm.-equivalent of OH to each grm.-equivalent of copper present. The following results show the changes with time in Solution III. above. The time was forty-eight hours. They also show that the excess of ammonia present did not stop these changes:—

Number of solution.	Concentration with respect to copper.	Ratio Cu : NH ₃ in solution.	Ratio Cu : H at time of permanent precipitation.	Ratio Cu : H at time of neutrality to methyl-orange.
III.	N 9.55	1 : 6.06	1 : 5.84	1 : 5.99
III.	N 9.55	1 : 6.06	1 : 5.80	1 : 5.96

These experiments were conducted with the greatest care. The flasks were carefully calibrated by weighing the water they contained at definite temperatures, and the burettes were calibrated by a method devised recently by one of us (*Am. Chem. Journ.*, 1903, xxx., 96). The solutions were made by weighing the flasks first dry and empty, and again after the salt had been introduced and the flasks

stoppered. Significant differences in temperature were corrected for.

The properties of solutions of the salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ indicate that the salt is decomposed by water with the partial separation of ammonia from the combination in which it is held by the salt in the dry condition (see 1, 2, and 3 above). This decomposition is probably an hydrolysis (see 6). In solutions of the pure salt it proceeds at least as far as the formation and precipitation of basic salts (see 2, 3, and 5). In solutions of the salts, even though they may contain an excess of ammonia, the concentration of hydroxyl ions undergoes changes throughout a considerable period of time (see 8). These changes are hastened or retarded by the removal or addition of ammonia (see 4 and 7), but the effects of the ammonia do not bear any simple relation to the concentration of the ammonia (see 8).

The formula $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ does not correctly represent the salt. If this formula were correct, the addition of 1 molecule of the salt to 4 equivalents of acid would produce a clear solution containing copper sulphate and ammonium salts and the products of their electrolytic dissociation, and would not produce a permanent precipitate (see 5).

VI. Summary.

1. We have shown the method of Fresenius and the "suggestion" of Küster and Thiel to be unreliable in the quantitative separation of sulphuric acid from copper. We have described a satisfactory method for the separation and for the determination of ammonia and water in a mixture of the vapours of the two. The conditions under which reliable results can be obtained in the complete analysis of cuprammonium sulphates have been worked out and have been stated.

2. The preparation of the salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ has been described, and a method of drying it and keeping it indefinitely in an analytically pure condition has been given. Its composition has been proved by complete analyses. Other products described as this cuprammonium sulphate by Mallaert and Bouzat have been shown to be mixtures. The method of drying hydrated cuprammonium salts over sticks of potassium hydroxide and a very little ammonia water, used recently by Kohlschütter, has been shown to alter the composition of the salts.

3. The properties of the pure dry salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ have been studied, and it has been shown that its molecular dissociation with loss of ammonia must be very slight. Its solubility at 21° to 22° C. has been determined. The action of dry ammonia upon the salt has been studied, and it has been shown that, under the given conditions, the replacement of the molecule of water in the salt by a molecule of ammonia, described by Latschinoff, does not take place without other reactions setting in, producing mixed products.

4. We have studied the behaviour of the salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ when heated at 100°, 125°, 149°, 203°, and 260° C., and have shown that the products in all cases were mixtures. The definite chemical compounds, $\text{CuSO}_4 + 2\text{NH}_3$ and $\text{CuSO}_4 + \text{NH}_3$, described by Kane, do not exist as such; if they are formed at all they are mixed with other products. We have studied the behaviour of pentahydrated copper sulphate at 78°, 100°, 220°, and 260° C., and have shown that the dehydration products were mixtures. We have shown that the action of ammonia on pentahydrated copper sulphate produces a mixture and that this is also true when ammonia acts on the salt $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$, even though both reactions take place at ordinary temperatures. We are of the opinion that a solid compound containing both copper sulphate and water cannot undergo change without other reactions between these two constituents taking place, giving rise to mixed products. For this reason, results of experiments on record in which solid hydrated compounds of copper sulphate have been heated, or treated with a gas, or changed in other ways (while still solid) are, *ipso facto*,

open to doubt. The most recent work to which this applies is that of Latschinoff.

5. Properties of aqueous solutions of the salt $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ have been described that show that the system $\text{CuSO}_4 + 4\text{NH}_3 + 11\text{H}_2\text{O} + x\text{H}_2\text{O}$, as found in a solution of the salt, is in an unstable condition, beginning with its existence to undergo a change that continues for a long time, and that it is in some cases not complete while the system remains homogeneous. The change which results in the precipitation of basic salts is hastened by the removal of ammonia and by great dilution. We have found that the change in the solutions can be followed readily by taking advantage of the facts that cuprammonium sulphate solutions titrated into acids give a definite end-reaction characterised by the formation of a permanent precipitate, and that copper sulphate solutions are practically neutral to methyl-orange indicator. The results obtained in this way do not permit of a satisfactory interpretation.

Because of the changes in solutions of this cuprammonium sulphate that continue for a considerable time, deductions of a general character, drawn from studies of cuprammonium sulphate solutions (in water), must be considered doubtful, except in cases where it has been shown that the measurements were made after equilibrium had been established in the solutions. The most recent work to which this applies is that of Dawson and McCrae and of Locke and Forsell.

PERCHROMIC ACID AND THE PERCHROMATES.*

By HORACE G. BYERS, University of Washington,
and
E. EMMET REID, Baylor University, Texas.

(Concluded from p. 100).

The Sodium Salt.—In the attempt to prepare the sodium salt in the same way as the potassium the difficulty was encountered that the compound which formed was closely adherent to the sodium, and was with difficulty separated from it. Particles of sodium caused trouble when the mass was put into the iron solution. The sodium salt thus prepared is similar in appearance to the potassium salt, but appears to decompose more easily, and at temperatures approaching zero assumes a pasty form. Analysis number 1, given in Table VI., is from the salt thus prepared.

It seemed probable that the substance prepared by Patten (*loc. cit.*) is this sodium salt. With this in view the blue ethereal solution was prepared cooled to -20° , and treated with powdered sodium acetate. A purple precipitate was formed mixed with the excess of acetate. The supernatant ether was found to contain acetic acid. It was shown by blank tests that the excess of acetate interfered in no way with our method of analysis. After decanting the ether and washing thoroughly with cold ether until the residue was free from the blue colour, samples were analysed with results appended:—

TABLE VI.

	Salt.	Chromate.	Ratio.
1	23.5	18.2	3.87 : 3
2	32.0	24.10	4.10 : 3
3	30.0	22.5	4.0 : 3
4	47.8	34.5	4.16 : 3
Mean			4.01 : 3

The Ammonium Salt.—An ammonium salt was prepared by passing gaseous ammonia into the blue ethereal solution cooled to about -40° . It is probably not necessary to work at such a low temperature, though one attempt to

prepare the salt at -10° was without result. The salt is a brownish yellow, and on analysis gave the results listed in Table VII. No attempt has yet been made to determine its relation to the salt prepared by Wiede and assigned the formula $(\text{NH}_4)_3\text{CrO}_4$:—

TABLE VII.

	Salt.	Chromate.	Ratio.
1	31.5	23.0	4.11 : 3
2	32.7	23.7	4.14 : 3
3	33.3	24.12	4.13 : 3
Mean			4.13 : 3

Other Salts.—By using the acetates of lithium, magnesium, calcium, barium, and zinc in the same way as in the case of the sodium, the corresponding salts of these metals were prepared. The magnesium and zinc salts acted only slowly upon the blue solution. All these compounds formed a chocolate-brown slurry with the excess of acetate and the ether used in washing. The analyses were carried out as in the other cases, except that in the case of the barium salt a solution of ferrous chloride was used as a reducing agent, and the solution was acidified with hydrochloric acid. All these compounds decomposed at the room temperature with the evolution of gas and the formation of yellow chromates. Table VIII. contains the results of the analyses:—

TABLE VIII.

	Lithium salt.	Chromate.	Ratio.
1	10.7	8.1	3.98 : 3
2	17.4	12.7	4.10 : 3
Mean			4.04 : 3

	Magnesium salt.	Chromate.	Ratio.
1	17.2	13.1	3.94 : 3

	Calcium salt.	Chromate.	Ratio.
1	27.4	19.5	4.12 : 3
2	25.3	19.5	3.94 : 3
3	36.5	27.5	3.98 : 3
4	36.5	28.1	3.83 : 3
Mean			3.97 : 3

	Barium salt.	Chromate.	Ratio.
1	24.1	18.1	3.98 : 3
2	25.3	19.25	3.94 : 3
Mean			3.96 : 3

	Zinc salt.	Chromate.	Ratio.
1	9.0	6.5	4.15 : 3
2	10.0	7.4	4.05 : 3
Mean			4.10 : 3

The average ratio of the oxidising power of all the salts to that of their chromium in the form of the chromate is 4.02 : 3.

These results point so clearly to the existence in the blue solution of an acid of the composition expressed by the formula HCrO_4 (or more probably $\text{H}_2\text{Cr}_2\text{O}_8$) that it was of interest to study the decomposition of the blue compound in the presence of alkalis.

The blue solution, prepared as in the previous experiments, was divided into four 50 c.c. portions. One of these was evaporated to dryness in a platinum dish, and the residue ignited and weighed as chromium oxide. The second and third were each placed in 250 c.c. of recently-boiled ice-cold water containing 50 c.c. of the standard iron solution and shaken vigorously in a separatory funnel, and the oxidising power determined.

* This work was begun at the University of Washington, and continued, jointly, at the University of Chicago, in the laboratory of General and Physical Chemistry. From the *American Chemical Journal*, xxxii., No. 5.

It was found that the ether interfered somewhat with the titration, by reason of surface phenomena, and hence a slight excess of the bichromate was added, and the solution boiled and cooled before completing the titration. The chromium was precipitated, fused, and re-determined as before. The fourth portion was placed in a Lunge nitrometer (capacity 150 c.c.) with 60 c.c. of dilute caustic soda, confined over mercury. After decomposition was complete the oxygen was determined by absorption in pyrogallol, after removal of the ether vapour. The alkaline solution was titrated against ferrous iron. Since several observers have shown, and as our own experience also shows, that there is a slight reduction below the bichromate stage of oxidation under these conditions, the chromium was re-precipitated, and again determined after fusion. The results are given in Table IX.

TABLE IX.

1. Cr_2O_3 found 0.0738 grm., equivalent to 29.10 c.c. N/10 bichromate.		
Blue solution.	Chromate.	Ratio.
2. . . . 40.1	30.4	3.96 : 3
3. . . . 39.6	29.166	4.01 : 3
4. Volume of oxygen (corr.) 6.5 c.c., equivalent to 11.61 c.c. N/10 bichromate.		

The alkaline solution was found equivalent in oxidising power to 27.5 c.c. bichromate, and after fusion to 29.54 c.c.

From the literature it appears that most of those who have worked upon this solution have used a large excess of hydrogen peroxide over that needed to effect the state of oxidation here indicated. It was then of interest to see if the presence of a known excess of hydrogen peroxide would affect the nature of the blue solution.

The solution was prepared as before, and afterwards shaken with an excess of 2.5 per cent hydrogen peroxide. The aqueous layer was separated, but the ether portion was not dehydrated. Portions of this solution were then analysed as before. Fifty c.c. of it contained 0.0682 grm. of chromic oxide corresponding to 26.88 c.c. N/10 bichromate. A second portion of 50 c.c., decomposed in the nitrometer as before, gave 10.05 c.c. oxygen, equivalent to 17.06 c.c. bichromate, while the re-fusion of the precipitated chromate showed itself equivalent to 22.1 c.c. Hence the ratio of the oxidising power of the blue solution to its equivalent chromate is as 5.44 : 3. A 50 c.c. portion of the solution, titrated directly against the iron in the former manner, gave as the oxidising power 62.9 c.c., and in the form of the chromate a value of 29.3 c.c.—a ratio of 6.4 : 3.

Attention is again called to the fact that this solution was not dehydrated, as that fact has perhaps a bearing on the question referred to in paragraph 3 of the summary.

Summary and Conclusions.

1. The experimental portion of this paper shows conclusively the existence of the perchromates, and that they have the general formula MCrO_4 , or $\text{M}_2\text{Cr}_2\text{O}_8$. The latter formula is perhaps more probable by reason of the analogous persulphates.

2. The blue solution, prepared without excess of hydrogen peroxide, contains the acid corresponding to these salts, i.e., $\text{H}_2\text{Cr}_2\text{O}_8$.

3. The results obtained by Moissan, Pechard, and by us when using a solution prepared with an excess of hydrogen peroxide all point to the probable existence of another compound possessing higher oxidising capacity. Whether this be true or not is a problem for which it is our hope to find the solution.

We are continuing this work, and hope to be able to prepare other salts of this acid, and to ascertain the relation of the acid and its salts to the other possible acids of chromium and its allied elements.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, February 24th, 1905.

Prof. J. H. Poynting, F.R.S., President, in the Chair.

A PAPER "On the Curvature Method of Teaching Geometrical Optics" was read by Dr. C. V. DRYSDALE.

The paper has been undertaken with the twofold object of giving a systematic exposition of the method of teaching elementary optics, which the author has found most suitable, and of giving an introduction to a subsequent paper on the treatment of aberrations by curvature methods. The physical curvature method is the simplest and most natural method of introducing the subject of optics to elementary students, and it may also be employed with advantage in more advanced work. The paper refers to some of the work which has already been done in this direction, and gives a classification of the various methods which have been used or proposed for attacking optical problems, the ordinary geometrical method being the only one which has been much used for lens problems in this country. Referring first to notation and units, curvature and angular units termed the dioptrie and the prism dioptrie have been adopted by ophthalmologists and opticians, and the author has proposed the use of multiples and sub-multiples of the former unit. Dealing first with elementary optics, a short account is given of the procedure which the author has found most suitable in actual teaching. The idea of curvature is introduced with its units and method of measurement, leading to the use of the sagitta as representing the curvatures of refracting and wave surfaces. In the case of reflection at a spherical surface, it has been found advantageous to restrict the terms positive and negative to convergent and divergent light respectively, independent of the foci being in front of or behind the surface. By this device the formulae for mirrors and lenses become identical. With respect to refraction, it has been found advisable to consider thin prisms and lenses as a whole, instead of dealing with the refraction at each surface separately, the formulae for such prisms and lenses being thus proved with greater simplicity. Cylindrical lenses and the properties of the combinations of two thin lenses are dealt with, and it is shown how the equivalent convergence, or power, and the positions of the principal or nodal points can be easily obtained by wave methods. In the second section of the paper, thick lenses and refracting systems are dealt with. The author uses the reduced distances of Gauss and extends the notation to curvature systems by adopting Gauss's convention of the reduced or equivalent thickness as the negative of the distance between two refracting surfaces divided by the refractive index of the medium, while the term reduced curvature is applied to the product of any curvature and the refractive index of the medium. The three Gauss relations are deduced by the curvature method, and by means of a simple inductual proof these relations are shown to hold for a system of any number of coaxial spherical surfaces.

It is then shown that the fundamental convergence formulae are immediately convertible, by multiplying the curvatures by the semi-aperture of the pencils, into the fundamental equations which Von Seidel has used for the tracing of a path of light through a system, and the section concludes with a table showing the comparison between the three methods of Gauss and Von Seidel and the curvature system.

The paper concludes with a short discussion of oblique refraction through a thin lens or combination of thin lenses in contact, showing how some of the results of more advanced geometrical optics can be readily obtained by curvature methods.

Prof. S. P. THOMPSON said he had brought before the Society two papers dealing with the curvature method in geometrical optics, one in 1888, and the other more recently

when he treated cylindrical lenses. Dr. Drysdale had pointed out that Herschel used the curvature method in 1827, but Prof. Thompson remarked that Herschel then put it forward tentatively, and finally abandoned it. Mr. Cheshire had recently shown that in 1857 Porro treated of teaching geometrical optics by curvatures, and it had been stated that the method was known to Galileo. He had, however, sought in vain for any reference to it in his writings. The curvature method was suggested to him in 1876, when Prof. Everett published a paper on C.G.S. units, and entered into the question of dimensions as an illustration of physical units. It was in an endeavour to extend the idea of dimensions to optics that he was struck with the fact that nearly every quantity was the reciprocal of a length, and that the ordinary formulae in connection with thin lenses and spherical mirrors simply meant that two curvatures could be added together directly to form a third. Thereupon, in 1878, he developed an elementary treatment of lens problems from this point of view, and that treatment he had taught since 1884. He had not gone far into the treatment of aberrations by curvature methods, but he had satisfied himself that it could be carried out. The author of the paper was to be congratulated upon linking the curvature method with the other methods of teaching geometrical optics, particularly that due to Von Seidel. With regard to some of the terms used by Dr. Drysdale, he thought the word "convergence" was unsuitable as it was apt to be confused with the angle between the limiting rays of a converging pencil. This angle was constant, but the convergence altered as the light approached the focus. Dr. Drysdale had used the term dioptrie as a unit of curvature. As a matter of fact, the term dioptrie was adopted by an International Congress held in Brussels in 1877 to represent the *power* of a lens of local length one metre. He thought the term prism dioptrie was an unfortunate one, and suggested prismoptrie in its stead. Prof. Thompson expressed his interest in the fact that the author proposed to deal with the aberrations of Von Seidel by the curvature method, and hoped that the treatment of astigmatism would be simplified. One advantage of the curvature method was that it simplified geometry, but its great advantage lay in the fact that it kept as nearly as possible to reality.

Mr. R. J. SOWTER, in advancing a friendly criticism of the paper, said that although a distinct contribution to the subject, the paper would probably make even more pessimistic those who felt that the curvature method in advanced optics was somewhat of a scare. This was directly opposed to the effect which Dr. Drysdale hoped for. The curvature method was suitable for the solution of many problems, mostly simple; but by its nature its intimate association with the spherical wave-front, it was so restricted in scope that it had to be discarded when we dealt with the modern problems of photographic optics and optical design. It was not proposed to labour any argument, merely to express an opinion, and in support of this he referred Dr. Drysdale to Dr. Hastings' "Light," appendix A, in which book would be found, amongst other things, the curvature method solution of the important Abbe-Helmholtz magnification equation deduced at length by Dr. Drysdale. The aberration problems to be treated in a second paper were awaited with interest. The position of scepticism taken up by Mr. Sowter as to the wholesale superiority of the curvature method was not removed by the paper, and in addition he was supported in such a pessimistic view by Mr. Cheshire, and by the assurance of a leading optical calculator and designer on the Continent, that for optical calculations the curvature method was of no use. In Germany, moreover, the method had been discarded.

Mr. T. H. BLAKESLEY said he agreed with Mr. Sowter that the curvature method was something of the nature of a will-o'-the-wisp. If a ray was looked upon as the normal trajectory of a wave surface, it was just as real as the wave surface; and in many cases it was quite as convenient to use rays as to use curvatures.

Mr. CHALMERS remarked that from his experience he had come to the conclusion that the curvature method was most effective for getting out approximate solutions to optical problems, but for fine design work it was not so good as the ray method. In dealing with problems from the point of view of least time, he proposed to borrow from the curvature method and its notation in order to simplify the labour in first design work. With regard to the term dioptrie he said it referred to the *power* of a lens. In order to avoid any ambiguity it might be called the *focal power* of a lens. He preferred the term "equivalent thickness" to that of "reduced thickness" used by the author, and said that it was unfortunate that Dr. Drysdale had followed the notation of Von Seidel and used the suffix -1 to denote the medium before the surface under consideration.

Dr. C. V. DRYSDALE, in reply, said that a good deal of attention had apparently been given to the subject, and that the speakers could be divided into two classes, the optimistic and the pessimistic. He would remain optimistic until he reached a point where the curvature method broke down. He had used the curvature method in dealing with the five aberrations of Von Seidel and also with achromatism, and he hoped to be able to bring the results of his investigations before the Society. A good deal might be said about the notation used in the curvature method, but he thought the method was preferable to others because it was easier to understand the physical processes involved.

Mr. R. J. SOWTER exhibited and described Dr. Meisling's Colour-patch Apparatus.

The apparatus is simple in its principle and construction, and is specially adapted for testing colour-blindness. Three incandescent electric lamps are employed, two large lamps and a small one. The two large lamps are enclosed in blackened boxes provided with ground-glass windows, the apertures of which are adjustable and measurable, and coloured-glass screens are mounted in front of these windows. If red and green are mixed, a red glass is placed in front of one window and a green glass in front of the other. These two colours illuminate the upper half of an opalescent glass window, which has its lower half illuminated by the white light from the third incandescent lamp, and is carried by an upright metal plate. This plate and the attached enclosing chamber for the third lamp are traversed by means of a screw and thumb-nut along a graduated scale parallel to the vertical plane containing the two coloured light sources. The intensity of illumination upon the screen, due to one of the coloured sources, is taken as inversely proportional to the square of the screen-source distance and directly proportional to the square of the cosine of the obliquity. As the small window travels along, the tint of its upper half passes from red to green, say, through a white colour which can be matched with that of the lower half, the intensity of the white illumination falling on the lower half of the window being varied by means of a sliding shutter. A normal eye adjusts the matching position to within 5 m.m., while an abnormal eye may disclose its abnormality by a deviation amounting to 5 c.m.

Dr. W. WATSON expressed his doubt as to the suitability of the apparatus for testing colour-blindness.

Dr. C. V. DRYSDALE said one of the chief difficulties in connection with colour-measurement was with regard to the size of the apparatus. It was necessary to bring three colours to the comparison patch, and long paths were necessary to get the requisite dispersion. The use of rotating sectors was a mechanical difficulty. In an apparatus which he had recently designed he had replaced rotating sectors by wedge-shaped strips formed by so exposing a photographic plate as to obtain a gradually increasing density. These wedges were placed in front of the slits, and the intensity of the transmitted light could be varied by altering the position of the wedge with regard to the slit.

Mr. J. SCHOFIELD read a paper on "A Method of Illustrating the Laws of the Simple Pendulum."

A pendulum is fitted at its lower end with a narrow horizontal framework carrying vertical transverse wires,

During the oscillations of the pendulum these wires are caused to cut a jet of mercury, and time signals are sent to the recording mechanism of a chronograph. The distances between the wires are known, and together with the time-measures they yield a displacement-time curve of the motion. From this the kinematical curves and equations of the moving system may be deduced by the usual methods. In the actual apparatus a tuning-fork arrangement with an accuracy of about $1/200$ of a second is used as the chronograph, and the results obtained from the pendulum are accurate to about 3 per cent. The principle has also been applied to torsion pendulums.

Mr. SCHOFFELD also exhibited a Set of String Models of Optical Systems, the lenses and prisms being made of celluloid, so that the paths of rays through them can be shown.

INSTITUTE OF CHEMISTRY.

THE Twenty-seventh Annual General Meeting was held at 30, Bloomsbury Square, on Wednesday, March 1st. Mr. DAVID HOWARD, President, in the Chair.

The Accounts for 1904 were submitted by Mr. A. GORDON SALAMON, Hon. Treasurer, and duly received.

Prof. FRANK CLOWES moved the adoption of the Annual Report of the Council, at the same time commenting on the progress of the Institute. He referred to the increase of 38 Members during the past year. The Register now contains the names of 973 Fellows and 163 Associates, making in all 1136 Members. The number of Candidates for the examinations had increased to such an extent that it was found necessary to hold both Intermediate and Final Examinations three times a year. After commenting on other matters in the Report, Prof. Clowes remarked on the growth of the Library. He hoped that the Fellows would continue to support it. Concluding, he said that the Institute was doing excellent work, and its qualifications and examinations were receiving more and more recognition. He was of the opinion that the time had come when the diploma of F.I.C. or A.I.C. should be insisted on, as evidence of competency, in connection with professional chemical appointments.

Mr. H. J. HELM, I.S.O., formally seconded the Report. Dr. G. T. MOODY said that he was disappointed to find no mention in the Report of the question as to the subjects of Preliminary Examination. He alluded particularly to the retention of Latin as a compulsory subject in the regulations of the Institute, and urged the Council carefully to consider the advisability of altering this regulation, which he believed detrimental to the interests of the Institute.

The PRESIDENT said that the question had been under the consideration of the Council, and he felt sure that it would be raised again. The Report was then formally received and adopted.

The ballot for the election of Censors having been taken, the following were declared elected:—Sir Thomas Stevenson, Prof. J. Millar Thomson, Prof. William A. Tilden, and Dr. John A. Voelcker.

The meeting then proceeded to appoint the Honorary Auditors, and Messrs. C. H. Cribb, R. E. Alison, and W. T. Burgess were appointed.

The PRESIDENT then delivered his Address. Before commenting on the matters which had engaged the attention of the Council during the past year, he referred to the loss the Institute had sustained by the death of several distinguished Fellows. He specially mentioned Mr. Alfred H. Allen, an earnest worker for applied chemistry, who had taken an active interest in the Institute since its foundation, and Mr. William Chattaway, who had for several years assisted in the examination work of the Institute. He remarked on the steady growth of the Institute, saying that he thought there was still a wide field for those possessing the highest chemical knowledge and skill, and that those who had to call in the aid of such knowledge and skill were becoming more and more alive

to the importance of employing only the properly trained and competent. He was of opinion that the training prescribed by the Institute, and the high standard of the examinations, had resulted in a decided improvement in the status of professional chemists. He emphasised the importance of requiring all candidates to produce evidence of a high standard of general education. The professional chemist should be a *professional* man as well as a chemist, and must therefore possess that general culture which is essential if he is to deal with his work in a professional spirit. He warmly supported the view hitherto held by the Council, that Latin should be retained as a compulsory subject in the preliminary examinations.

Referring to the position of the Institute in connection with the Sale of Food and Drugs Acts, he mentioned that 94 per cent of the Public Analytical appointments were held by Fellows of the Institute. He drew the attention of the members to the memorial presented by the Association of Public Analysts of Scotland to the Local Government Board (Edinburgh). They had been obliged to draw the attention of the Board to the fact that a number of authorities in Scotland were in the habit of submitting test samples to persons whose qualifications had not been approved by the Board, which practice was not calculated to secure the proper administration of the Acts.

The Government of India and the India Office had considered communications made to them by the Institute with reference to the practice of professional chemistry in India. The President drew the attention of the Fellows to a resolution recently passed by the Government, in which the qualifications F.I.C. and A.I.C. were formally recognised for public analytical appointments in India. The Council had undertaken to consider under what conditions officers of the Indian Medical Service could be admitted to the examinations of the Institute.

The President proceeded to deal with other matters mentioned in the Report, and alluded to the action of the Board of Agriculture in encouraging provincial technical and agricultural colleges to undertake professional chemical work gratuitously, or at purely nominal fees. In their endeavour to help dairy farmers, the Board had induced the colleges, which are maintained by grants for technical education for the benefit of a particular class, to compete with professional chemists, particularly those retained by the agricultural associations, at the expense of the general public. The colleges needed the grants for the promotion of the education of farmers in the science and practice of agriculture without diverting them to other purposes. It was for them to instruct the farmers in agricultural chemistry. It was certainly not the business of the colleges to do work for farmers, and if the latter could get work done for nothing, or next to nothing, they would not be likely to do it for themselves. If farmers are to have free analysis, why not let them have free veterinary and medical advice? His traction-engines should be sent to the engineering department of the college. But the farmers were not the only people who contribute to the Education Grants. Why should not the smith have gratuitous analysis of his iron, the dyer of his dyes, the druggist of his drugs, and so forth? Why should we not all be fed with pap—at the public expense—with a Government spoon? The President also mentioned that, in connection with the Fertilisers and Feeding Stuffs Act, 88 per cent of the District Agricultural analytical appointments were held by Fellows of the Institute. In conclusion, he reminded the members that if they might congratulate themselves on the present position of the Institute, they should not lose sight of the fact that much of its success was due to those who had worked for it in its early history. They had realised that, much as chemists had done for the world in the past, still greater things must be done by them in the future, and an organisation such as the Institute should tend to draw them together to work for the common good.

On the motion of Prof. J. MILLAR THOMSON, seconded Dr. JOHN A. VOELCKER, a cordial vote of thanks was accorded to the President for his Address.

The Officers and Members of Council for the ensuing year were duly elected as follows:—

President.—David Howard.

Vice-Presidents.—Edward John Bevan; Edward Divers, M.D., D.Sc., F.R.S.; Percy Faraday Frankland, LL.D., Ph.D., F.R.S.; Edmund Albert Letts, D.Sc.; Edmund James Mills, D.Sc., F.R.S.; John Millar Thomson, LL.D., F.R.S.

Hon. Treasurer.—Alfred Gordon Salamon, A.R.S.M.

Members of Council.—Bertram Blount; Lt.-Col. Charles Edward Cassal; Alfred Chaston Chapman; Arthur Crozier Claudet, A.R.S.M.; John Norman Collie, Ph.D., F.R.S.; James Kear Colwell; James Johnstone Dobbie, M.A., D.Sc.; Bernard Dyer, D.Sc.; Martin Onslow Forster, D.Sc., Ph.D.; Richard John Friswell; William Gowland, A.R.S.M.; Arthur George Green; Oscar Guttmann; Henry James Helm, I.S.O.; James Hendrick, B.Sc.; Egbert Grant Hooper; Herbert Jackson; William Walker James Nicol, M.A., D.Sc.; William Jackson Pope, F.R.S.; Alexander Scott, M.A., D.Sc., F.R.S.; William Ashwell Shenstone, F.R.S.; Alfred Smetham; Arthur Smithells, B.Sc., F.R.S.; David Alexander Sutherland; Edward William Voelcker, A.R.S.M.; William Palmer Wynne, D.Sc., F.R.S.; Sydney Young, D.Sc., F.R.S.

With a vote of thanks to the retiring Officers and Members of Council for their services, moved by Mr. THOMAS TYLER and seconded by Mr. ARTHUR E. EKINS, the proceedings terminated.

CORRESPONDENCE.

LICENCE FOR LABORATORY STILLS.

To the Editor of the Chemical News.

SIR,—With reference to the letters under the above heading in your issues of February 24th and March 3rd (CHEMICAL NEWS, vol. xci., pp. 95 and 105), it may be well to direct the attention of your readers to the following letter received by the Institute of Chemistry from the Board of Inland Revenue in 1892:—

DEAR SIR,—Having laid before the Board of Inland Revenue your letter of the 28th July, I am directed, in reply, to acquaint you for the information of the Council of the Institute of Chemistry that the Board have no desire to extend the obligation to take out a licence to analytical chemists using stills solely for purposes of distilling water. If an analytical chemist called upon to take out a licence by one of the Board's officers will submit his case to the Board, they will be prepared to give it careful consideration.—I am, Sir, your obedient servant,

(Signed) W. B. HEBERDEN, Asst. Sec.

Copies of the above letter were sent at the time to various chemical journals, and I believe it was published in the CHEMICAL NEWS. It was not considered quite satisfactory, and further representations were made to the Board, with the result that they issued instructions to the officers of the Board that professors, teachers of chemistry, and analytical chemists should be allowed the use of stills for purely professional work in all cases in which no manufacture of any article for sale from or with spirit is carried on.—I am, &c.,

RICHARD B. PILCHER,
Registrar and Secretary.

Institute of Chemistry,
30, Bloomsbury Square, London, W.C.,
March 6, 1905.

Electrolysis of Organic Acids by Means of an Alternating Current.—André Brochet and Joseph Petit.—The electrolysis of formic and oxalic acids can be easily effected by the alternating current. The results are the same as with a continuous current, but the yields are much greater.—*Comptes Rendus*, clx., No. 7.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxl. No. 6, February 6, 1905.

Synthesis in the Anthracene Series. Symmetric Tetraalcoyldiamide. Derivatives of γ -Tetraphenylanthracene Dihydride.—A. Haller and A. Guyot.—The authors obtain the condensation products of symmetric γ -diphenyl- γ -dihydroxyl anthracene dihydride with dimethylaniline and diethylaniline by heating or cooling equimolecular quantities of these two compounds in acetic solution. The condensation is effected in two phases, characterised by successive tints, which are seen when a few drops of the acetic solution are poured into concentrated sulphuric acid. Finally, after prolonged ebullition, the liquor dissolves in sulphuric acid without appreciable colour. The condensation is then finished.

The Three Methylcyclohexanones and their corresponding Methylcyclohexanols.—Paul Sabatier and A. Mailhe.—The three methylcyclohexanones have hitherto been prepared by various methods, always complicated. The best known of these products, methylcyclohexanone-1.3, is fairly easily prepared by hydration of pulegone. By treating the solution in aqueous ether by means of sodium the corresponding alcohol is obtained. It is also known that the three cresols—ortho, meta, and para—lend themselves, in the same way as phenol itself, to MM. Sabatier and Senderens' method of hydrogenation. By this means the three corresponding methylcyclohexanols can be prepared. The authors use this reaction to obtain the alcohols. They then investigate their properties, as well as those of the derived acetones.

Direct Fixation of Ethero-organo-magnesium Derivatives on to the Ethylenic Liaison of the Non-saturated Ether Salts.—E. E. Blaise and A. Courtot.—The authors' series of experiments show that the organo-magnesium derivatives can be directly fixed on to the ethylenic liaison, but the fixation demands the presence of an electro-negative group in a corresponding to the double liaison. In the case of the acyclic iodides, it is apparently limited to the iodide of magnesium methyl, and consequently, from the theoretical point of view, this interesting reaction only seems capable of practical application in exceptional cases.

Cryoscopy of Sulphates.—Albert Colson.—An investigation of the cryoscopy of sulphates shows that there are certain complications which prove that in the relation $n = \lambda N$, which connects the numbers n and N of the gaseous and liquid molecules of the dissolved body, the value of λ is not the same as in the corresponding relation between the molecules n' and N' of the solvent. Then, according to M. Mathias, the gaseous molecules—which are the only ones known—cannot be substituted for the unknown liquid molecules in the general formula of cryoscopy.

New Method of Detecting Ammonia. Application to Water Analysis.—MM. Trillat and Lurchet.—The reaction of nitrogen iodide can be utilised in many cases for the detection of ammonia. It is specially applicable in discovering the purity of waters and detecting the pollution of water by decomposing organic matter.

Evolution of Carbon in Natural Combustible Substances.—Isidore Ray and Just Alix.—The proportion of carbon increases during the transformation of cellulose into graphite, whilst the other elements (oxygen, hydrogen, &c.) diminish. The nitrogen does not follow this law, and, by the authors' curve of the evolution of nitrogen, it will be seen that this element, which is absent in cellulose, increases during the change from wood to peat, and finally diminishes normally. The authors intend further to investigate this irregular presence of nitrogen.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 6th inst., His Grace The Duke of Northumberland, K.G., D.C.L., F.R.S., President, in the Chair. Mr. W. K. Appleton, Dr. G. H. Burford, Mr. W. S. Burns, Mrs. Close, Miss Donaldson, Dr. G. E. Haslip, Lady Hodgson, Mrs. Lave, Mr. J. B. Tapling, Lieut.-Col. Vincent Wing, C.B., Mr. P. von Fleischl, and Mr. J. E. Wolfe were elected Members.

New Atlas of Emission Spectra of the Elements.—The publication of an authorised English edition of the new Atlas of Emission Spectra of most of the Elements, by A. Hagenbach and H. Konen, with text translated by Dr. S. A. King, of the Carnegie Institution, will be welcomed by all students of the subject. The Atlas consists of 28 plates, heliographic reproductions, and will be issued at a low price. W. Wesley and Son, 28, Essex Street, Strand, are the publishers, where a proof copy of the plates may now be seen.

The Blue "Adsorption" Compound given by Iodine with the Basic Acetate of Lanthanum.—W. Biltz.—Dannour observed in the year 1857 (*Comptes Rendus*, vol. xliii., p. 970) that the gelatinous precipitate formed in the cold by ammonia in a solution of acetate of lanthanum, is coloured blue by iodine in the same manner as starch. The author has examined this phenomenon very closely. The colouration only disappears by heating. If the solutions are very dilute no precipitate is formed, but simply a colouration. The very dilute solution of acetate of lanthanum being made slightly alkaline with ammonia, then submitted to dialysis, gives first of all a clear solution, then a coagulum of the colloidal sub-acetate. Both are coloured by iodine. The author has made certain by means of numerous quantitative experiments that no definite compound is formed. As with starch, we have to do with a compound of "adsorption" given by the iodine when mixed with a colloidal substance.—*Berichte*, vol. xxxvii., p. 719.

MEETINGS FOR THE WEEK.

- MONDAY, 13th.—Society of Arts, 8. (Cantor Lecture). "Telephony," by Herbert Laws Webb, M.Inst.C.E.
- TUESDAY, 14th.—Royal Institution, 5. "Some Recent Biometric Studies," by Prof. Karl Pearson, F.R.S.
- WEDNESDAY, 15th.—Microscopical, 8. "Review of Work done by Metallographers" (illustrated by Lantern Slides), by J. E. Stead, F.R.S.
- Society of Arts, 8. "Methods of Design in Mohammedan Art," by E. H. Hankin, M.A.
- Chemical, 5.30. "Velocity of Oxime Formation in certain Ketones," by A. W. Stewart.
- "Catechin and Acacatechin," by A. G. Perkin.
- "Action of Ethyl Dibromopropanetetracarboxylate on the Disodium Compound of Ethyl Propanetetracarboxylate," by W. H. Perkin, jun.
- "On Glutaconic Acid, and the Conversion of Glutaric Acid into Trimethylenedicarboxylic Acid," by G. Tatarsall.
- "The Ultra-violet Absorption Spectra of certain Enol-keto-tautomers," by E. C. C. Baly and C. H. Desch.
- "Esterification Constants of Substituted Acrylic Acids," by J. J. Sudborough and D. J. Roberts.
- "Chloro-cinnamic Acids," by J. J. Sudborough and T. C. James.
- "Di-ortho-substituted Benzoic Acids—Part VI, Conversion of Methyl into Ethyl Esters," by J. J. Sudborough and T. H. Davies.
- "Simple Method for the Estimation of Acetyl Groups," by J. J. Sudborough and W. H. Thomas.
- "Gynocardin, a New Cyanogenetic Glucoside," by F. B. Power and F. H. Lees.
- THURSDAY, 16th.—Royal Institution, 5. "Recent Astronomical Progress," by Prof. H. H. Turner, F.R.S.
- Society of Arts, 4.30. "Manipul and its Tribes," by T. C. Hodgson, late I.C.S.
- FRIDAY, 17th.—Royal Institution, 9. "Dramatic Thoughts—Retrospective, Anticipative," by Sir Squire Bancroft.
- SATURDAY, 18th.—Royal Institution, 3. "Electrical Properties of Radio-active Substances," by Prof. J. J. Thomson, F.R.S., &c.

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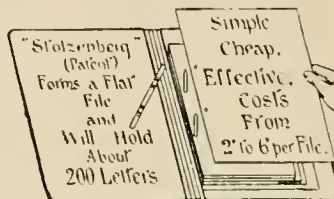
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THE CHEMICAL NEWS.

VOL. XCI., No. 2364.

THE RADIO-ACTIVITY OF THORIUM.*

By F. ZERBAN.

SOME time ago in an article on "Radio-activity and Matter" (*Berichte*, 1904, xxxvii., 1655) Clemens Winkler (who has since died) disputed the proof brought forward by K. A. Hofmann and the author (*Berichte*, 1903, xxxvi., 3093, 3911) of the presence of uranium in monazite sand. In the article in question he says:—"F. Zerban . . . thinks that he has proved the presence of a small quantity of uranium in monazite sand, which has hitherto been supposed to be free from uranium. However, objection may be made to the method of research used by him, which originated with Laube, and was meant originally, not for analytical purposes, but for the working up of uranium residues."

Now it already appeared from my paper that Laube's method was naturally not used by me to *prove* the presence of uranium, but to *separate* the uranium, on the one hand, from iron, and on the other from phosphoric acid. The *proof* of the presence of uranium depended obviously upon its characteristic reactions with ammonia and with potassium ferrocyanide, which seemed to exclude the possibility of its being confused with other substances. Since it was actually possible by means of these reactions to discover uranium in the filtrate from the phosphate precipitate, objections to Laube's method of separation could not invalidate this proof.

Consequently, I asked Herr Winkler by letter to define his objections. He answered:—"I do not at all doubt the correctness of the proof you have brought forward of the occurrence of uranium in monazite, but wished to convey the idea that monazites containing no uranium must occur also."

At the same time, Winkler requested Prof. Brunck, of Freiburg, to examine for uranium the phosphate liquors obtained in the Drossbach Fabrik, during the working up of monazite sand. Prof. Brunck most kindly undertook this task. He used Rose's old method for separating the phosphoric acid, *i.e.*, fusion with potassium cyanide and some soda, by which means any uranium present was converted into uranoso-uronic oxide. Prof. Brunck wrote me that he found uranium in this phosphate liquor, and that in his estimation it amounted to about 0.1 per cent of the original material. This agrees with the numbers I found, which ranged from 0.02 to 0.1 per cent.

Thus up to the present all monazite sands which were specially tested for uranium were found to contain it. The next question was whether this uranium only adhered to the minerals mixed with the monazite, or whether monazite itself contains uranium. The examination of a beautifully crystallised Norwegian monazite provided a proof of the latter alternative. After separation of the phosphoric acid by Rose's method I could detect about 0.02 per cent of uranoso-uronic oxide. The thorium from the mineral was radio-active. This is a fresh proof of the fact discovered by K. A. Hofmann and the author, that those minerals which yield radio-active thorium also contain uranium.

On the other hand, according to our earlier investigations, inactive thorium resulted from minerals containing no uranium. (See also Charles Baskerville and F. Zerban, "Inactive Thorium," *Journ. Am. Chem. Soc.*, 1904, xxvi., 1642). The conclusion we drew that thorium in itself possesses no radio-activity was confirmed by Charles

Baskerville (*Journ. Am. Chem. Soc.*, 1904, xxvi., 922) on the basis of totally different observations.

If a radio-active thorium should be found in a monazite sand containing no uranium, there is in this case the possibility of induction by radium. Haitinger and Peters (*Sitzungsber. der K. K. Akad. der Wissensch. Wien, Mathem.-naturw. Kl.*, Bd. cxiii., Abth. IIa., May, 1904) have already proved the occurrence of this substance in monazite sand.

Meanwhile, the whole question of the radio-activity of thorium has entered upon a new stage. The suggestions made by Chronstchoff (*Journ. Russ. Phys. Chem. Gesellsch.*, xxix., 206; *Chem. Zeitung*, 1890), Auer von Welsbach (*CHEMICAL NEWS*, lxxxv., 255; *Journ. f. Gasbeleuchtg. u. Wasservers.*, 1901, 661), and Brauner (*Proc. Chem. Soc.*, 1901, xvii., 67) that thorium is not a simple element, has been confirmed by Baskerville's researches (*loc. cit.*). Sir William Ramsay ("The Present Problems of Inorganic Chemistry," a lecture delivered at the International Congress of Arts and Sciences at St. Louis, 1904) has also recently expressed doubts as to the elementary nature of thorium.

Up to the present it has been established that all the three chloride fractions obtained by Baskerville's method after being converted into oxide emit α - and β -rays. The activity is somewhat concentrated in those fractions with higher atomic weight, but the differences are only very small (Baskerville, *loc. cit.*; see also F. Zerban, "On the Complexity of Thorium," a lecture delivered at the Annual Meeting of the American Association for the Advancement of Science, Philadelphia, December, 1904). No more definite conclusions can be drawn from this, but the continuation of the researches will no doubt lead to further discoveries with regard to this question.

I wish to thank Prof. Brunck, who, as well as Herr Winkler, showed the keenest interest in the question discussed here, for his kindness in performing these experiments, and also for his valuable communications. I also wish to express my thanks to the Carnegie Institution for their assistance.—*Berichte*, 1905, xxxviii., 557.

RADIO-TELLURIUM.

IV.*

By W. MARCKWALD.

By the kindness of the proprietor of the chemical works of Dr. Rich. Sthamer, in Hamburg, a quantity of raw tellurium, which had been separated from 5 tons of Joachimsthal uranium residues, corresponding to about 15 tons of pitchblende, was placed at my disposal. The separation had been performed in essentially the same way as I have described previously, namely, by precipitation with stannous chloride from the solution of bismuth chloride first obtained.

This precipitate still contains various impurities. To purify it it is dissolved in dilute nitric acid, the solution filtered and evaporated, and the residue repeatedly evaporated with hydrochloric acid to drive off the nitric acid; it is then taken up with dilute hydrochloric acid, and sulphurous acid is introduced into the solution. A precipitate is thus formed, consisting of a mixture of selenium, tellurium, and radio-tellurium. Hence it follows that the chloride of radio-tellurium, like TeCl_4 , is reduced by sulphurous acid, while, as was shown before, it differs from tellurium chloride in its behaviour towards hydrazine.

On precipitating with sulphurous acid it was observed that the radio-tellurium separates with relatively the greatest difficulty; since from a solution containing selenium and tellurium the selenium was first precipitated by the reduction agent, radio-tellurium fits into the series of the periodic system as regards this property also.

The weight of the precipitate amounted in all to 16 grms.

* Published with the consent of the Carnegie Institution.

* *Berichte*, 1902, xxxv., 2285, 4239; 1903, xxxvi., 2662.

The method of separation by means of hydrazine previously described was found less convenient than another method. The radio-tellurium oxide has not the property of an acid anhydride, as may be deduced if we assume that it occupies its supposed position in the periodic system of the elements. It is known that even tellurous acid is so weak an acid that it forms no stable ammonium salt, though it dissolves easily and copiously in excess of ammonium hydroxide. The oxide of radio-tellurium, on the other hand, is quite insoluble in ammonia solution.

Hence for the separation of the radio-tellurium the precipitate obtained on addition of sulphurous acid was dissolved in dilute nitric acid, the solution evaporated to dryness, and the residue warmed with ammonia solution. A very small residue remained, and could be collected on the filter. Its weight amounted to about 3 m.grms. Nevertheless, it represented the whole yield of radio-tellurium, for the tellurium separated from the solution was comparatively only very feebly radio-active.

Obviously the activity of the substance collected on the filter was enormous. Judging by the yield its purity far exceeded that of the product obtained before. Nevertheless, there was no guarantee that this substance was perfectly pure, as the cost of the material precluded a further chemical examination.

In spite of the smallness of the quantity in which radio-tellurium is contained in pitchblende, the separation by the method described above is so simple and reliable that it is not difficult to prepare it. As for most physical investigations, thousandths of a m.grm. are sufficient, and for all demonstration purposes hundredths of a m.grm., apart from the chemical examination, it is not difficult to get sufficient of this substance.

For nearly a year I have been occupied in investigating the question whether radio-tellurium retains its activity lastingly, or whether the effect diminishes. I thought I had previously observed a decrease of activity in the substance deposited on the bismuth rod. But as these little rods contained, according to the present state of our knowledge, only thousandths of a m.grm. of active substance, the decrease of their activity could be ascribed to mechanical influences.

The precipitates produced later with the pure substance were so active that rough tests revealed no diminution. Yet the copper plate which I described in my last communication on this subject, and upon which there was only 1.100 m.grms. of radio-tellurium, after it had been used for, two years, still excited the phosphorescence screen sufficiently to make the luminescence distinctly visible at a distance of 10 to 15 metres.

However, exact experiments have proved the decrease of activity of radio-tellurium. Thus a new confirmation is adduced of Rutherford and Soddy's disaggregation theory, according to which a radio-active element must lose its activity the more rapidly the more active it is.

The results of this investigation, in which Drs. Grunacher and Hermann took part, and which was carried out in the Physical Institute of this University, will be reported in full elsewhere. But as Dr. Stefan Meyer and Dr. Egon v. Schweidler, as I learn from a reprint from the *Akademische Anzeiger*, No. XXV., kindly sent me by the authors, have communicated an investigation dealing with the same question to the Kaiserliche Akademie der Wissenschaften in Vienna at the meeting of December 1st of last year, a preliminary account of the result of our experiments will be given here.

First of all, it is to be noted that our experiments were performed with an exceedingly small quantity of radio-tellurium (at the most of the order of magnitude of 1/1000 m.grms.); the material had been purified by the above method, and was precipitated on a silver plate, while Meyer and v. Schweidler used commercial bismuth rods or copper plates. Their experiments extended over three months, ours over ten months. It is thus not remarkable if the results of the two series of investigations do not agree perfectly. However, the agreement is very fair. It shows

that my first method of separation gave radio-tellurium free from any other radio-active substance however much it might be adulterated with other inactive substances.

The saturation current provided the standard for the strength of the radio-activity in both investigations. From the provisional publication of Meyer and v. Schweidler, which only contains a few lines, the time in which the radiation intensity of radio-tellurium sinks to half its value, based upon the most reliable series of observations, amounts to 135 days. "The decay approximately occurs according to the law $e^{-\lambda t}$."

We also found that the decay follows the formula for monomolecular reactions, as is to be expected for elementary radio-active substances. The following table shows how far the values calculated according to the formula—

$$\frac{J_t}{J_0} = e^{-\lambda t}$$

agree with our observations. The value of λ was calculated to $\lambda = 0.004959$, taking into account all the observations, t being expressed in days.

No. of days.	$J_t : J_0$	
	Calculated.	Found.
70	0.707	0.725
97	0.608	0.591
128	0.530	0.514
260	0.276	0.265
319	0.206	0.210

Thus the intensity falls to half its value in 139.8 days, and the mean duration of existence of the radio-tellurium atom is 201.7 days.

The constant of radio-activity is the characteristic mark of a radio-active substance. Further investigations, which are still being continued, lead to no material change in the value given here. It is thus proved that radio-tellurium is an elementary radio-active substance, and, contrary to the opinion constantly expressed, it is not identical with "polonium." Without doubt the Curie's "polonium" contained radio-tellurium, which I have proved is also present in Giesel's polonium. It is equally certain that "polonium" is a mixture of radio-active substances. In her famous dissertation, Mme. Curie makes the following statement regarding the decay of her polonium:—"A sample of nitrate lost half its activity in eleven months and 95 per cent in thirty-three months. Other specimens behaved similarly. A sample of the metal lost 67 per cent of its activity in six months." The two first numbers show that this polonium must have contained more than one radio-active constituent, because the decay did not occur according to the formula for monomolecular reactions. The last number given, in contrast to the two first, shows a more rapid decay than radio-tellurium, which loses 67 per cent of its activity in seven and a-half months.

The relatively stable transformation product of radium, RaE, discovered by Rutherford (*Phil. Mag.* 1904, viii., 636; *Phil. Trans.*, 1904, cciv., 202), the activity of which sinks to half its value in a year, is shown by the investigation of Meyer and v. Schweidler, as well as by our experiments, not to be identical with radio-tellurium. On the other hand, the decay constant agrees remarkably with one of the above values, which Mme. Curie has repeatedly observed with her bismuth-polonium nitrate.—*Berichte*, 1905, xxxviii., 591.

Non-existence of Two Stereoisomers of Ethyl Dioximidobutyrate.—L. Bouveault and A. Wahl.—The authors perform a series of experiments and find that only a single ethyldioximidobutyrate exists, which melts at 162° , and that the proofs of the existence of the two stereoisomers apparently shown by Hantzsch and Nussberger rest solely on analytical and experimental errors.—*Comptes Rendus*, cxi., No. 7.

"GLUCINUM" OR "BERYLLIUM."

By JAS. LEWIS HOWE.

SOME years ago the question of choice between the two names "glucinum" and "beryllium" was gone into quite carefully by Prof. F. W. Clarke, and also by the committee appointed by the American Association on the Spelling and Pronunciation of Chemical Terms, and the conclusion was arrived at that the name "glucinum" should be used on the ground of priority. In *Science* for December 9 (see also CHEMICAL NEWS, xci., 75) Dr. Charles Lathrop Parsons has stated his grounds for preferring the name "beryllium." Dr. Parsons is, thanks to his bibliographical work on the element in question, thoroughly informed in its literature, but the arguments adduced by him would seem to lead to a conclusion diametrically opposed to that which he has drawn.

It was obviously the privilege of Vauquelin, the discoverer of the element, or rather its oxide, to name it. This he never did, but contented himself by speaking of it at first as "la terre du Béril," that is, the earth in beryl. At the close of Vauquelin's first paper the editors of the *Annales* added a note signed "Redacteur" in which they propose the name "glucine." It was of course well known that Guyton and Fourcroy were the editors. Vauquelin's second paper in the *Annales* was evidently prepared at the same time as the first, or at least before the second was in print. In his third paper, some weeks later, as Dr. Parsons admits, Vauquelin actually adopted the term "glucine," prefacing its use with "on a donné le nom de glucine." The paper in the *Journal des Mines* was apparently prepared at the same time as the first two papers in the *Annales* and before the appearance of the suggestion of Guyton and Fourcroy, but at its close occurs the note which Dr. Parsons has quoted. In this he states that Guyton and Fourcroy have advised him to call the new earth "glucine," and while he evidently does not think the name the best that could have been chosen, he clearly acquiesces in the suggestion of the two great authorities, and says, "Cette denomination sera assez significative pour aide le mémoire." Finally, as seen above, in his third paper, he adopts the name. As far as priority goes, the argument in favour of "beryllium" would seem to be that probably Vauquelin would have given the earth some other name had he ventured to dissent from Guyton's authority, and it is probable that he would have liked to name it "beryllia." All of which may be quite true, but actually he did not do it.

As regards the German use of "Berylerde" it was merely at first the natural translation of Vauquelin's expression "la terre du Béril," which, as we have seen, he used in no denominative sense. If the generally accepted rules of priority have any weight, "glucinum" is the only term to be used for the element.

As regards usage, the case is hardly quite as bad as Dr. Parsons seems to think, since the index to the *Journal of the Chemical Society* for 1903 gives "Beryllium, see glucinum." With French, English, and Americans using "glucinum," we can afford to let the German journals cling to "beryllium" a little while longer.

Incidentally, what shall we do when the Germans insist on kalzium, kolumbium, karolinum, zerium, and zesium, or will it be kasium?

Washington and Lee University.
December 12, 1904.

"BERYLLIUM" OR "GLUCINUM."†

By CHARLES LATHROP PARSONS.

THERE is apparently little difference of opinion between Dr. Howe and myself as to the facts upon which a claim to priority of "beryllium" over "glucinum" as a name for the element under discussion is based, and I am willing to leave the interpretation of those facts to chemists at large.

It has, I think, been supposed by those of the profession who have not personally looked into the matter that the oxide was named "glucine" by Vauquelin himself. I understand that Dr. Howe in his reply to me in *Science* for January 6, admits that Vauquelin did not name the element or the oxide; that he in fact would probably have liked to name it "beryllia," really adopting glucine in his fourth publication under virtual protest, and that the clause "la terre du Béril" used by Vauquelin in place of a name was literally translated into German as "Berylerde" becoming a definite name, used to this day, before Vauquelin consented to the use of "glucine." I think also that he will not question the fact that when it came to the actual use of the terms themselves, that Wohler separated and described "beryllium" (*Ann. der Phys.*, xiii., 577) before Bussey prepared "glucinum" (*Journ. de Chim. Medical*, iv., 453), although they were but a few weeks apart. With this summary I am perfectly willing to leave the question of priority to the "ninety and nine" who are already using the more preferable term.

As to usage it is quite evident that Dr. Howe's closing remarks are intended as a pleasantry, as I hardly think he wishes to give the impression that kalzium, kolumbium, &c., are the custom in German chemical literature. He does not question that the major part of the literature is German, nor that the Germans, Swedes, Danes, Russians, Dutch, and Italians use "beryllium" exclusively. Next to the Germans the French have the most articles to their credit, and use "glucinum" exclusively, but the impression which Dr. Howe seems to wish to convey that this is the customary term in England and America is not correct. He made a lucky find in the index of the *Journal of the Chemical Society* for 1903, which does read "Beryllium, see Glucinum" for some unknown reason, for the one abstract to which it refers uses "beryllium" solely both in title and subject matter, and "glucinum" does not appear in this journal in index or abstracts on the subject for several years previously, although the abstracts are frequently from the French. This journal apparently leaves the matter to the wishes of the author, for Pollock, in 1904, uses again glucinum. For at least five years the term "beryllium" has been used exclusively in the index of the *Journal of the Society of Chemical Industry*, and so far as I have noticed in the subject matter as well. On the other hand, the CHEMICAL NEWS uses the two words interchangeably in its articles, abstracts, and index, part of its articles being indexed under one head and part under the other, and, unfortunately, without any attempt at cross reference. In America only one original article has appeared on the subject in many years which has used "glucinum." The *American Chemical Journal* has used "beryllium." The *American Journal of Arts and Sciences* for some years has used "beryllium," and it is here that some of the best articles have appeared. The *Journal of Physical Chemistry* uses "beryllium." The *Journal of the American Chemical Society* has allowed its contributors to choose, and one article and two abstracts have appeared on "glucinum" since its publication.

To play on Dr. Howe's own words, I think that with American, English, German, Swedish, Danish, Dutch, Russian, Italian, &c., journals and chemists using "beryllium" we can afford to let the French cling to "glucinum" (not "glucium") a little while longer.

It is true that the committee appointed by the American Association on the Spelling and Pronunciation of Chemical Terms did recommend "glucinum," and so far as I can find its members are about the only American chemists loyal to the term. I think it highly unfortunate that their recommendations as to spelling and pronunciation have not been more generally adopted in our chemical literature and language, but it is true they have not, and in regard to "glucinum" it is my humble opinion that they were wrong.

New Hampshire College.
January 23, 1905.

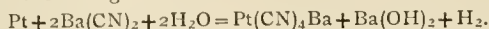
* *Science*, January 6, 1905.
† *Science*, February 17, 1905.

ELECTROLYTIC PREPARATION
OF PLATINOCYANIDE OF BARIUM.

By ANDRÉ BROCHET and JOSEPH PETIT.

THE production of platinocyanide of barium has assumed a peculiar interest of late years on account of the use of this salt for the manufacture of screens for use with X-rays and radio-active substances.

The chemical methods at present in use are long and complicated; therefore we have made use of the solution of platinum in cyanide of barium under the influence of an alternating electric current. The reaction brought about is the following one:—



According to this, 40 parts of the metal (38.3, to be exact) give directly 100 parts of the platinocyanide, $\text{Pt}(\text{CN})_4\text{Ba} \cdot 4\text{H}_2\text{O}$. No other salt of platinum is formed, but the cyanide of barium is partially oxidised with the formation of carbonate of barium and ammonia on the one hand, and nitrate of barium on the other. We have experimented on a certain number of operations, which have led us eventually to the following practical method; we give the figures obtained during the course of one of these operations.

Apparatus.—We used a flask of 1 litre capacity, closed with an indiarubber stopper having four holes in it. Three of these are for the passage of the electrodes and a thermometer. In the fourth, situated in the centre, is fitted the stem of a funnel containing a plug of glass-wool for the purpose of arresting any of the solution carried off mechanically by the hydrogen. This tube will also allow the passage of a stirring-rod; to the funnel we can also fit a tube enabling us to collect and wash the gases.

The electrodes are formed of strips of platinum 5 c.m. by 10 c.m. and 0.1 c.m. in thickness; these are soldered to platinum wires 0.34 c.m. in diameter and 20 c.m. in length. They are plunged to a depth of 9 c.m. into the solution of which we give the composition lower down.

The strength of the current used is 20 ampères. Under these conditions the apparatus becomes warm fairly rapidly; to prevent any great loss of the salt through the mechanical action of the hydrogen, the flask is placed in a glass dish of 3 litres capacity full of tepid water. The temperature of the whole apparatus is then kept at about 50–60°.

Preparation of the Electrolyte.—Cyanide of barium is not met with commercially; it is prepared in a very simple manner, and its solution keeps well if it is made alkaline; further, this is the best condition to have it in for purposes of electrolysis. On account of the slight solubility of hydrate of barium in the cold, it is easily prepared under the necessary conditions; for 1 litre of a 10 per cent solution of hydrocyanic acid, we require 750 grms. of hydrate of baryta. Solution takes place with a lowering of the temperature; the operation is easily done in the following manner:—The above mentioned quantity of hydrate of baryta is placed in a flask of 1500 c.c. capacity; we add 100 c.c. of hydrocyanic acid, and heat on the water-bath to warm up the mixture. A fresh portion of acid is then added, and so on, until the whole of the baryta is in solution. Then the remainder of the acid is added all at once. The final volume of the solution is about 1300 c.c.; after filtration the solution deposits the excess of baryta it contains. It is now ready for use, and will keep indefinitely, colourless and limpid. This solution contains about 270 grms. of cyanide, $\text{Ba}(\text{CN})_2$, per litre.

Method of Procedure.—For each operation we use 750 c.c. of solution of cyanide. Under the influence of the current the liquid becomes hot. When the temperature is about 50° the outer vessel is filled, as has been mentioned, and the operation goes on quickly. After eight hours the current is stopped, an abundant deposit of carbonate of barium is formed; on cooling, the greater part of the platinocyanide of barium is crystallised.

In this operation about 35 to 40 grms. of platinum are dissolved, which corresponds to about 100 grms. of the salt.

The almost complete decomposition of the cyanide of barium can be effected by passing the current for twenty-four hours, but the return is much lower, as we only get about 60 grms. of platinum into solution; that is, 150 grms. of the salt. The difference of potential between the two poles of the apparatus remains almost constant at about 5 volts. It rises slightly if we attempt to decompose the whole of the cyanide.

Chemical Treatment.—The contents of the apparatus are turned into a large flask, the wash-waters added, and the whole diluted to 2 litres. Heat on the water-bath while passing a current of carbonic anhydride, so as to saturate the baryta and completely destroy the cyanide of barium. The solution is filtered with a filter-pump, and the precipitate washed several times with boiling water, and the whole of the filtrate is concentrated down to about half a litre. Under these conditions almost the whole of the platinocyanide crystallises out on cooling.

The mother-liquors are evaporated to dryness, and the residue taken up with warm methylic alcohol, which dissolves the platinocyanide and leaves the nitrate of barium. When the alcoholic solution is evaporated a further quantity of the salt is obtained.

If we desire to prepare large quantities of the product, it will be found advantageous, from the point of view of the return obtained, to stop the current after eight hours and allow the solution to crystallise. The magma, formed of platinocyanide, carbonate of barium, and hydrate of baryta, should be drained, dissolved in water, and treated as has been just described. The filtered liquid, treated with baryta and hydrocyanic acid, is ready for further electrolysis. We might also, during the electrolysis or before crystallisation, saturate the baryta formed by means of hydrocyanic acid. But in every case the electrolysis must be made with a solution containing an excess of the free base, otherwise the solution will become black.

Fluorescent Platinocyanide of Barium.—The platinocyanide obtained in the manner just described is yellow, it has a slight dichroism, and under the influence of radium, for example, it is slightly fluorescent. It is easy to give it the fluorescence necessary for the manufacture of screens. We have observed that the simplest method is to crystallise the product in a solution of cyanide, cyanide of barium, for example. By cloudy crystallisation we obtain small green crystals which are very fluorescent. The mother-liquor will serve for several operations, and can be used finally as the primary solution. The product retains its fluorescence after re-crystallisation.

According to Dammer ("Handbuch der Anorganischen Chemie") the green product contains an excess of cyanide of barium, and answers to the formula $\text{Pt}_5(\text{CN})_{22}\text{Ba}_6, 22\text{H}_2\text{O}$. Given this formula, we considered it necessary to try whether the property of being fluorescent or not corresponded with any difference in the formula of the salt.

With this object we made the following estimations:—

	Ba.	Pt.
	Per cent.	Per cent.
a. Fluorescent product, first crystallisation	27.1	—
b. Fluorescent product, re-crystallised ..	26.9	38.1
c. Non-fluorescent product	26.9	39.1
d. Commercial fluorescent product ..	27.1	—
$\text{Pt}(\text{CN})_4\text{Ba}_4\text{H}_2\text{O}$	27.0	38.3
$\text{Pt}_5(\text{CN})_{22}\text{Ba}_6, 22\text{H}_2\text{O}$	29.8	35.6

The result of these analyses shows that we have to do with two varieties of the same salt, and that the formula $\text{Pt}_5(\text{CN})_{22}\text{Ba}_6, 22\text{H}_2\text{O}$ must be discarded.

Expenditure of Energy.—An instrument placed across the poles of our transformer showed an expenditure of energy of fifteen kilowatt-hours per kilogram. of platinocyanide. This is small compared with the value of the product and with the present conditions of its preparation.

This valuation, however, is really much above the truth on account of the low efficiency of our transformer and the absorption of energy by the regulating rheostat.

We found that the energy calculated from measurements made by an ammeter and a voltmeter, is at the most eight kilowatt-hours per kilogram of platinocyanide. *Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 23.

A NEW GENERAL COLOUR REAGENT OF THE POLYPHENOLS, THEIR ISOMERS, AND HIGHER ORGANIC COMPOUNDS.

By Dr. EUGENE PINERUA ALVAREZ,
Professor of General Chemistry of the Faculty of Science of Madrid.

THE new reagent of the polyphenols and their isomers is the hydrate of sodium dioxide, $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$, formerly called hydrate of peroxide by Vernon Harcourt, until Joannes and Tafel discovered respectively in 1893 and 1894 the trioxide of sodium, Na_2O_3 , of a pale pink colour, and its hydrate, $\text{Na}_2\text{O}_3 \cdot \text{H}_2\text{O} = 2\text{NaO}(\text{OH})$, bodies which are really the true peroxidised compounds of the said metal.

The substances which produce the hydrate used as reagent are—Sodium dioxide, $\text{Na}_2\text{O}_2 = 2\text{NaO}$; ether, or pure anhydrous ethyl alcohol ($D = 0.797$); and cold or cooled water.

The following have been the means employed for detecting the polyphenols:—

In a little porcelain basin of 30 c.c. capacity were placed 0.20 gm. of yellow, granulated, perfectly dry sodium dioxide, immediately afterwards 0.04 or 0.05 gm. of the polyphenol to be tested, and then 5 c.c. of absolute alcohol.

These substances are allowed to remain in contact with one another from four to six minutes (according to the surrounding temperature); whilst the reaction is taking place the liquid is kept in motion by imparting a slight circular movement to the basin; and, finally, 15 c.c. cold distilled water is added.

If we had added the water before the alcohol, at the ordinary temperature, the mixture of polyphenol and dioxide would have ignited.

The colourations observed were as follows:—

Hydroxyphenol-1.2. or *Pyrocatechin* = $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O.H.1} \\ \text{O.H.2} \end{smallmatrix}$ —

The alcohol immediately acquires a *transitory pale pink* colour, which changes after five or six minutes into *green*, and finally turns *brown*. On wetting the inner surface of the little basin with the pink liquid and blowing the edge of the spot, which is hardly visible, this surface acquires a *blue-green* colour. On adding water, the liquid becomes a very permanent *red-brown*.

Hydroxyphenol-1.3. or *Resorcin* = $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O.H.1} \\ \text{O.H.3} \end{smallmatrix}$ —The alcohol immediately assumes a *very pale yellow* colour, and after five or six minutes becomes *greenish*. On adding water, the *green* colour deepens and becomes permanent.

Hydroxyphenol-1.4. or *Hydroquinone* = $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O.H.1} \\ \text{O.H.4} \end{smallmatrix}$ —The alcohol assumes immediately a *very intense reddish yellow* colour. On damping the inner surface of the little dish with the coloured liquid, which is very adhesive, and then blowing on the spot, its edges acquire a *transitory blue* colour. By the addition of water, a liquid of a very persistent *orange* colour is obtained.

Dihydroxyphenol-1.2.3. or *Pyrogallol* = $\text{C}_6\text{H}_3 \begin{smallmatrix} \text{O.H.1} \\ \text{O.H.2} \\ \text{O.H.3} \end{smallmatrix}$ —

The alcohol immediately assumes a *reddish brown* or *dull red* colour. Then, by adding water, it becomes an *intense red* with yellow edges. Twenty-four hours after, the liquid is *orange*.

Dihydroxyphenol-1.2.4. or *Oxyhydroquinone*, $\text{C}_6\text{H}_3 \begin{smallmatrix} \text{O.H.1} \\ \text{O.H.2} \\ \text{O.H.4} \end{smallmatrix}$ —The alcohol assumes at once a *reddish violet* shade. The violet shade is clearly perceptible in the spot of red liquid on the inside surface of the porcelain

dish. After a few moments (four or five minutes), the dioxide deposited at the bottom of the little dish is seen to acquire a *black* colour, and the supernatant liquid loses its original colour, deepens, and turns *brown*. On adding water, the resultant liquid tints the surface of the dish *yellow*.

Dihydroxyphenol-1.3.5. or *Phloroglucine* = $\text{C}_6\text{H}_3 \begin{smallmatrix} \text{O.H.1} \\ \text{O.H.3} \\ \text{O.H.5} \end{smallmatrix}$ —The alcohol immediately assumes a *blue-violet* colour.

By the addition of water the *violet* colour increases in intensity for some time, becoming *very beautiful*, but soon slowly fades. At the end of twenty-four hours the liquid is almost colourless.

Methylhydroxyphenol-1.3.5. *dihydroxytoluene*, or *Orcine* = $\text{C}_6\text{H}_3 \begin{smallmatrix} \text{C.H}_3.1 \\ \text{O.H.3} \\ \text{O.H.5} \end{smallmatrix}$ —The alcohol immediately

assumes an intense pink shade, especially the phenol which is in contact with the dioxide. After adding water, the *rose-red* colour persists. The liquid has the appearance of a strong infusion of the petals of the *Rose rubra*.

Methylhydroxyphenol-1.3.4. *methylpyrocatechin*, or *Homopyrocatechin*, $\text{C}_6\text{H}_3 \begin{smallmatrix} \text{C.H}_3.1 \\ \text{OH} \\ \text{OH} \end{smallmatrix}$ —The alcohol at once

assumes a *blue-violet* tint, which changes immediately to *red*. On damping the edges of the little china dish, the edges of the spot assume a *greenish yellow* colour by contact with the air. By the addition of water, the liquid becomes *reddish brown* with yellow edges.

Isopropyl-4-methylhydroxyphenol-1.2.3. or *Thymohydroquinone* = $\text{CH}_3 \begin{smallmatrix} \text{CH}_3.1 \\ \text{CH}_3 \end{smallmatrix} > \text{C}_4\text{H} - \text{C}_6\text{H}_2 \begin{smallmatrix} \text{O.H.2} \\ \text{O.H.3} \end{smallmatrix}$ —The alcohol

immediately assumes an intense *orange* colour. On wetting the inner surface of the china dish, a deep *yellow* stain is produced. By the addition of water the liquid becomes *wine-red* and slowly loses its colour.

Notes.

All the polyphenols tested were as follows:—*Pyrocatechin* comes from the firm of Messrs. Ludwig Ellon and Co., Charlottenberg.

Resorcin and *pyrogallol* resublime, very white; from the firm of Messrs. Merck, Darmstadt.

Absolutely pure *hydroquinone* and very pure *phloroglucine* (free from di-resorcin) were obtained also from the firm of Messrs. Merck, Darmstadt.

The *oxyhydroquinone*, *orcine*, *homopyrocatechin*, and *thymohydroquinone* came from the works of C. A. Kahlbaum, Berlin.

The *dihydroxyphenol-1.2.4* was considerably changed.

We tested a small quantity (a specimen) of *hydroxyphenol-1.2*, also from the same factory, and the results were identical with those from the firm of Ludwig Ellon, Charlottenberg.

The alcohol immediately assumed a *transitory pale pink* colour. Only we notice that it lasts longer than that obtained from Ludwig's *pyrocatechin*. A little longer time must be allowed for it to become brown. By the addition of water we also obtained the permanent *reddish brown* liquid with yellowish edges.

Royal Institution.—On Tuesday next, March 21, at 5 o'clock, Prof. W. E. Dalby delivers the first of a course of two lectures on "Vibration Problems in Engineering"; Mr. Thomas G. Jackson, B.A., will on Thursday next, March 23, at 5 o'clock, deliver the first of his course of two lectures on "The Reasonableness of Architecture"; Prof. Meldola will give the first of his two lectures on "Synthetic Chemistry" (Experimental) on Thursday, April 6. The Friday Evening Discourse on March 24 will be delivered by Sir Oliver Lodge, his subject being "A Pertinacious Current," and on March 31 by Prof. J. Wright on "The Scientific Study of Dialects."

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, March 2nd, 1905.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

MESSRS. Robert J. Caldwell, Edward Evans, Lewis Eynon, and E. J. Fairhall were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. John George Baxter, Court Sole, Cliffe, near Rochester, Kent; Roger Dodds, Bigods Hall, Dunmow Essex; Sydney Dunstan, 107, Jesmond Road, Newcastle-on-Tyne; Albert Gillies, Government Laboratories, Johannesburg, S. Africa; Henry Isaac Gorman, 126, Quay, Waterford; Ernest Green, 113, Hulton Street, Moss Side, Manchester; John Hawthorne, 7, Roseneath Villas, Military Road, Cork; Arthur Lonsdale Hetherington, B.A., Government Collegiate School, Rangoon, Burma; Sydney A. Kay, D.Sc., 72, Market Street, St. Andrew's; Leonard Gibbs Killby, B.A., 10, Aberdeen Park, Highbury, N.; Ernest Isaac Lewis, B.A., B.Sc., Felstead School, Felstead; Alfons O'Farrelly, M.A., 3, Holles Street, Dublin; William Sarginson, B.Sc., 200, Cauldon Road, Stoke-on-Trent; Robert Reed Swann, B.Sc., The Agricultural College, Aspatria, Cumberland.

Of the following papers, those marked * were read:—

*24. "*The Relation between Natural and Synthetical Glycerolphosphoric Acids.*" By FREDERICK BELDING POWER and FRANK TUTIN.

Glycerolphosphoric acid was first prepared synthetically by Pelouze (*Comptes Rendus*, 1845, xxi., 718; and *Journ. Prakt. Chem.*, 1845, xxxvi., 257), who, from the analyses of some of its salts, concluded that it was identical with that obtained from lecithin.

By the interaction of glycerol and phosphoric acid, it is possible that several esters may be formed, and three of these are now known, namely, the mono-ester, or glycerolphosphoric acid, $C_3H_5(OH)_2 \cdot O \cdot PO(OH)_2$; the so-called di-ester, $C_3H_5(OH) \cdot \overset{O}{\underset{O}{\parallel}} PO(OH)$; and the tri-ester, $C_3H_5 \cdot PO_4$.

The authors have shown that the discrepancies of statement respecting the composition and characters of the salts of glycerolphosphoric acid (compare Portes and Prunier, *Journ. Pharm. Chim.*, 1894, xxix., 393; Petit and Polonowsky, *Ibid.*, 1894, xxx., 193; and Adrian and Trillat, *Ibid.*, 1898, vii., 226) are due, as has been suggested by Carré (*Comptes Rendus*, 1903, cxxxvii., 1070), to their contamination with salts of the above mentioned di-ester. It was therefore deemed of interest to ascertain the characters of the salts of glycerolphosphoric acid when prepared under such conditions as are known to exclude the formation of the di-ester, and a number of these have been described and analysed.

In the course of the authors' work, Willstätter and Lüdecke described an investigation (*Ber.*, 1904, xxxvii., 3753) in which they compared the barium and calcium salts of the natural and synthetical glycerolphosphoric acids, and came to the conclusion that the differences between them are not those which are usually observed in the case of optically active and racemic compounds. These differences consisted in the amount of metal contained in the respective salts, in the varying amounts of water believed to be retained by them when dried at certain temperatures, and in their relative solubility in water.

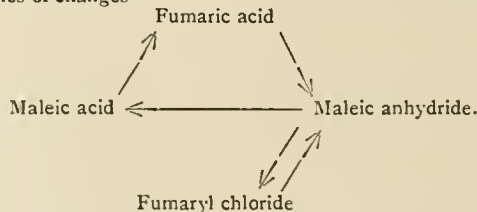
The authors have shown, however, that the conclusions of Willstätter and Lüdecke are not valid, inasmuch as their synthetical glycerolphosphoric acid was prepared under conditions which are known to afford some of the di-ester, and that the discrepancies they have observed are to a large extent due to the contamination of their salts of

the synthetical acid with those of the di-ester rather than to the amount of water retained by them when subjected to heat.

The fact was also noted that the natural glycerylphosphoric acid has in no instance been prepared from a lecithin which was known to be a pure individual substance. Although the preparations obtained from this source by Willstätter and Lüdecke possessed optical activity, which proved the presence of the unsymmetrical acid, no evidence can as yet be adduced that they did not contain some of the symmetrical isomeride.

*25. "*The Transmutation of Geometrical Isomerides.*" By ALFRED WALTER STEWART.

In order to explain this series of phenomena, the author assumes as a phase of the reaction the formation and disruption of a tetramethylene compound. In the case of maleic and fumaric acids, the intermediate compound would be a tetramethylene-1:2:3:4-tetracarboxylic acid, in which, probably, the carboxyl groups attached to the 1:2-carbon atoms would lie on the side of the ring opposite to those attached to the 3:4-atoms. Such a tetramethylene ring might split up in two ways; either by breaking the linkings between 1 and 2, 3 and 4; or by breaking those joining 1 to 4 and 2 to 3. In the former case, fumaric acid is formed; in the latter, maleic acid is regenerated. If, however, fumaric acid is produced, owing to its higher melting point, it is immediately withdrawn from further action, while maleic acid is free to undergo the same series of changes. Fumaric acid, when distilled in presence of phosphoric oxide, is assumed to form the same type of tetramethylene derivative; but in this case water is abstracted from the carboxyl groups attached to the 1:2-carbon atoms, and also from those attached to the 3:4-atoms, the groups in each pair being in the *cis*-position to one another. Owing to the presence of the two anhydride chains, the tetramethylene ring cannot now break across in either of two ways, as in the last case, and consequently its disruption produces maleic anhydride. The complete series of changes—



can be thus explained; and also the transformations undergone by stereoisomeric oximes, hydrazones, and diazo-compounds. The author gives instances in which the tetramethylene intermediate product has actually been isolated, when it is found that its behaviour fulfils the conditions required by the hypothesis.

DISCUSSION.

Dr. COLMAN pointed out that tetramethylene-mono- and dicarboxylic acids are very stable substances, and that it therefore hardly seemed probable that the tetramethylene-tetracarboxylic acid, assumed by the author to be the intermediate product between fumaric acid and maleic anhydride, would be so readily resolved quantitatively into two molecules of maleic acid.

*26. "*Linin.*" By JAMES STEWART HILLS and WILLIAM PALMER WYNNE.

According to Pagenstecher (*Buchner's Repert. Pharm.*, 1840, lxxii., 311; 1842, lxxvi., 313; 1843, lxxix., 216) and Schröder (*Neues Repert. Pharm.*, 1861, x., 11), purging flax (*Linum catharticum*), a small indigenous herb, contains a substance, linin, to which the former investigator attributed the purgative properties of the drug.

The authors believe the active principle to be a glucoside, which, however, has not been isolated in a pure state owing to its uncrystallisable nature. On hydrolysis with

dilute acids or with lime, the glucoside is resolved into glucose and a substance which, so far as the comparison can be made, seems to be identical with Schröder's linin. The yield of crude linin amounts to about 0.13 per cent by weight of the drug.

Linin, $C_{23}H_{24}O_9$ (mol. wt. 445 and 451 in naphthalene; 453 and 437 by the boiling point method in acetone), crystallises from alcohol in needles, and melts at about 203°, the exact melting point depending on the mode of heating; it is insoluble in water, sparingly soluble in the usual organic solvents, and gives a deep purple coloration with concentrated sulphuric acid. It contains four methoxyl groups, as determined by the Zeisel method; the demethylated derivative proved to be uncrystallisable. Attempts to prepare acetyl and benzoyl derivatives of linin were fruitless, and inconclusive results were obtained by fusion with caustic potash. Oxalic acid was the only recognisable product when it was oxidised with nitric acid or potassium permanganate under varied conditions. Linin is destitute of purgative properties.

*27. "The Constitution of Phenylmethacridol." By JAMES JOHNSTON DOBBIE and CHARLES KENNETH TINKLER. When phenylacridine methiodide is treated with an alkali, a hydroxide is formed which was supposed at one time to be the base corresponding with the original salt. Hantzsch, however, from the results of conductivity experiments, concluded that it is really a carbinol formed by the shifting of the hydroxyl group from the nitrogen atom to an adjacent carbon atom at the moment of precipitation. Confirmation of this view is afforded by the fact that whilst the absorption spectra of phenylacridine methiodide and of the hydroxide derived from it differ widely, the spectra of the latter substance agree very closely with those of dihydrophenylacridine. This resemblance is inexplicable, unless we regard the hydroxide as a carbinol bearing the same relation to dihydrophenylacridine that cotarnine bears to hydrocotarnine or hydrastinine to hydrohydrastinine (*Trans.*, 1903, lxxxiii., 598; 1904, lxxxv., 1005).

28. "The Ultra-violet Absorption Spectra of certain Diazo-compounds in Relation to their Constitution." By JAMES JOHNSTON DOBBIE and CHARLES KENNETH TINKLER.

The authors have applied the spectroscopic method to the investigation of isomerism in the diazo-group. They find that the stable and unstable forms of the isomeric diazophosphonates and of the isomeric diazocyanides derived from *p*-anisidine and *p*-chloroaniline give identical spectra, or spectra agreeing more closely than those of any isomerides which differ structurally from one another. They regard this result as affording confirmation of the correctness of Hantzsch's view, according to which these substances are *syn*- and *anti*-modifications, differing from one another in the same way as the *syn*- and *anti*-oximes. On the other hand, the isomeric potassium benzenediazotates, as also the two forms of the potassium compound obtained from diazotised sulphanilic acid, give widely different spectra. The spectra of the more stable (Schraube and Schmidt's) potassium benzenediazotate are almost identical with those of phenylmethylnitrosoamine, from which the authors infer that these compounds are constituted alike and are represented respectively by the formulæ $C_6H_5 \cdot N \cdot K \cdot NO$ and $C_6H_5 \cdot N(CH_3) \cdot NO$.

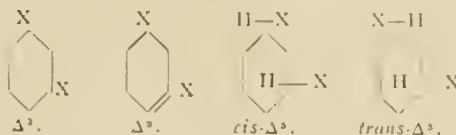
29. "The Latent Heat of Evaporation of Benzene and some other Compounds." By JAMES CAMPBELL BROWN.

An improved apparatus has been employed in determining exactly the latent heat of benzene and its homologues. The latent heats of *tert*.-amyl alcohol and propyl isobutyrate are also recorded, together with Trouton's values (compare *Trans.*, 1903, lxxxiii., 987).

30. "The Reduction of isoPhthalic Acid." By WILLIAM HENRY PERKIN, jun., and SAMUEL SHROWDER PICKLES.

When isophthalic acid is reduced with sodium amalgam at 45°, it yields two tetrahydro-acids (Δ^2 and *cis*- Δ^3), and, from these, two further acids are obtained by the methods

mentioned below. Since there can only be four tetrahydro-isophthalic acids, namely,—



it follows that the authors have been successful in isolating all the possible modifications.

Δ^2 -Tetrahydroisophthalic acid melts at 168°, is very soluble in water, and is characterised by yielding a rather sparingly soluble calcium salt and an anhydride which melts at 78°; it combines with hydrogen bromide and with bromine to form 2-bromohexahydroisophthalic acid (m. p. 185—187°) and 2:3-dibromohexahydroisophthalic acid (m. p. 202°) respectively. When oxidised first with permanganate and then with chromic acid, it yields succinic acid.

Δ^3 -Tetrahydroisophthalic acid is produced when the other tetrahydroisophthalic acids are boiled with strong caustic potash, intramolecular change taking place; it melts at 244° and is very sparingly soluble in water. When it is digested with acetic anhydride and then distilled, it is converted into the anhydride of the Δ^2 -acid. It combines with hydrogen bromide with difficulty, yielding a syrup which appears to be 4-bromohexahydroisophthalic acid and readily absorbs bromine vapour with formation of 3:4-dibromohexahydroisophthalic acid (m. p. about 230°). The latter acid is decomposed by boiling with caustic potash, with formation of a dihydroisophthalic acid which melts at 255° and is very sparingly soluble in water. When the Δ^3 -tetrahydro-acid is oxidised with permanganate or with nitric acid, it yields isophthalic and oxalic acids.

cis- Δ^4 -Tetrahydroisophthalic acid melts at about 165°, is very readily soluble in water, and, when digested with acetic anhydride and distilled, yields the anhydride of the Δ^2 -acid. It combines with bromine, with formation of 5:6-dibromo-*cis*-hexahydroisophthalic acid, which melts at about 220°.

trans- Δ^4 -Tetrahydroisophthalic acid is produced when the *cis*-acid is heated with hydrochloric acid at 170°. It melts at 225—227°, is very sparingly soluble in water, and combines with bromine to form 5:6-dibromo-*trans*-hexahydroisophthalic acid, which decomposes at about 230—235°.

The reasons which have led the authors to assign to the various tetrahydroisophthalic acids the constitutions given above are discussed in the detailed paper.

31. "The Influence of Temperature on the Interaction between Acetyl Thiocyanate and certain Bases. Thiocarbamides, including Carboxy-aromatic Groups." By the late ROBERT ELLIOTT DORAN (compiled by AUGUSTUS EDWARD DIXON).

Miquel's acetyl thiocyanate (*Ann. Chim. Phys.*, 1877, [5], xi., 293), when brought into contact at low temperature with aniline dissolved in benzene, showed little sign of thiocarbimide character, the principal change being the following double decomposition:— $AcSCN + 2PhNH_2 = PhNH_2 \cdot HSCN + AcNHPh$. On the other hand, when these materials were caused to interact at higher temperatures, the thiocyanic character diminished and the thiocarbimide reaction increased, until, in the neighbourhood of 85°, about 90 per cent of the additive compound (acetylphenylthiocarbamide) was obtained, according to the equation $AcNCS + PhNH_2 = AcNH \cdot CS \cdot NHPh$.

With *o*-toluidine this was not the case, an experiment conducted at 85° giving 91 per cent of the available sulphur in the form of acetyl-*o*-tolylthiocarbamide, whilst at -3° the yield of this substance was only a few per cent less.

By combining acetyl thiocyanate with methylaniline in hot benzene, acetylmethylphenylthiourea was obtained in white crystals melting at 93—94°. Acetylphenylbenzyl-

thiourea separated from dilute alcohol in fine rhombic crystals melting at 110–111°. Piperidine gave no acetyl-piperidylthiourea, but piperidylthiourea instead, together with piperidyl thiocyanate; the former melted at 126–127°, the temperature given by Wallach (*Ber.*, 1899, xxxii., 1872), and by treatment with acetic anhydride yielded the acetyl derivative, $\text{AcN:C(SH)·NC}_5\text{H}_{10}$ (long prisms melting at 112–113°). By passing ammonia gas through a boiling solution of acetyl thiocyanate in benzene, 21 per cent of the available sulphur was obtained as acetylthiourea, AcN:C(SH)·NH_2 .

Phenyl chlorocarbonate, PhO·COCl , when dissolved in benzene and left in contact with potassium thiocyanate until free from halogen, gave a solution of *carboxyphenylthiocarbimide*; by treatment with methylamine, this afforded *carboxyphenylmethylthiocarbimide*, PhO·CO·NH·CS·NHMe (long glistening prisms melting at 175–176°), isomeric with the author's carboxymethyl-phenylthiocarbimide, MeO·CO·NH·CS·NHPh , m. p. 158° (*Trans.*, 1901, lxxix., 908).

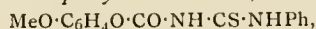
Carboxyphenylisoamylthiocarbimide is a crystalline solid (m. p. 99–100°) isomeric with *carboxyisoamylphenylthiocarbimide* (*loc. cit.*, 914).

Phenylcarboxyphenylthiocarbimide,—



was obtained (a) from aniline, and (b) by expelling, by means of phenyl chlorocarbonate, the acetyl-group from acetylphenylthiocarbimide; it melted at 148–149°.

Carboxyguaiacolphenylthiocarbimide,—



from guaiacol chlorocarbonate and acetylphenylthiocarbimide, melted at 154–155° and was freely desulphurised by warming with alkaline lead solution.

32. "The Influence of Solvents on the Rotation of Optically Active Compounds. Part VIII. Ethyl Tartrate in Chloroform." By THOMAS STEWART PATTERSON.

Data relative to the rotation of ethyl tartrate in chloroform at various concentrations and temperatures are given. Chloroform has a marked effect in depressing the rotation of the ester. It is shown that the variation of rotation is in agreement with the change in solution-volume of the dissolved tartrate.

33. "A Further Note on the Addition of Sodium Hydrogen Sulphite to Ketonic Compounds." By ALFRED WALTER STEWART.

The author has applied the method already described (*Trans.*, 1905, lxxvii., 185) to some other compounds containing the carbonyl group.

The rate of addition of sodium hydrogen sulphite to ethyl acetoacetate having already been found to be much more rapid than was anticipated, it was thought advisable to try experiments with diethyl acetonedicarboxylate. The results were as follows:—

After to	20	30	40	50	60	70	minutes.
40·2	55·3	61·0	64·5	68·1	71·2	73·0	

per cent of bisulphite compound.

Comparing this with the numbers already found in the cases of acetone and ethyl acetoacetate, it appears that the replacement of hydrogen by a carboxyl group increases the velocity of addition, and when a second carboxyl group is introduced instead of another hydrogen atom, the velocity is further accelerated. This seemed to point to the addition of sodium hydrogen sulphite to the carboxyl group itself, but when this hypothesis was tested by determining the addition of sodium hydrogen sulphite to ethyl acetate, no interaction could be detected.

Diacetylacetone and acetylacetone were also tried, one equivalent of sodium hydrogen sulphite solution for each carbonyl group present being used. The percentages for each carbonyl group were:—

Bisulphite compound-	After 10	20	30	40	50	60 minutes.
Diacetylacetone ..	14·6	17·8	21·3	23·9	26·3	27·8 per cent
Acetylacetone ..	5·7	8·8	11·5	14·6	16·6	19·5 "

Potassium β -camphorsulphonate, prepared by Reychler's method (*Bull. Soc. Chim.*, 1898, [3], xix., 120) gave a constant value of 3·5 per cent.

The figures for maltose, glucose, and lactose are:—

	After 10	20	30 minutes.	
Maltose ..	2·6	2·9	3·1	per cent of bisulphite compound
Glucose ..	5·2	5·2	5·2	" "
Lactose ..	7·7	8·4	9·0	" "

Unsuccessful attempts to prove the existence of additive products were made with epichlorhydrin, carbamide, acetamide, formamide, allyl alcohol, and ethyl cinnamate. Dimethylpyrone gave traces of some additive compound, but concordant results were not obtained.

34. "Action of Hydrogen Peroxide on Carbohydrates in the presence of Ferrous Sulphate." Part V. By ROBERT SELBY MORRELL and ALBERT ERNEST BELLARS.

In this communication, attempts have been made to trace the disappearance of different sugars during their oxidation by observing the decrease in the rotation angle, and from the determination of the initial and final reducing powers of the solutions, as well as their acidities, to obtain a fuller knowledge of the many oxidation stages which occur. The results of the change in the optical activity show that during successive additions of hydrogen peroxide up to 1 grm.-molecule for the same weight of carbohydrate, the decrease in the angle is proportional to the amount of oxidising agent added. The relative diminution in the angle depends on the sugar oxidised; galactose shows a greater decrease than glucose or fructose, maltose less than sucrose, which, in turn, has a smaller decrease than lactose. Rhamnose becomes laevorotatory on oxidation, and the rotation is practically constant after 2 grm.-atoms of oxygen have been added. The high values of the final reducing powers must be due to the strong reducing powers of keto-acids and osones formed in the oxidation. The acidities of the solutions after oxidation are not large, and are insufficient to account even for the complete formation of one monobasic hexose acid.

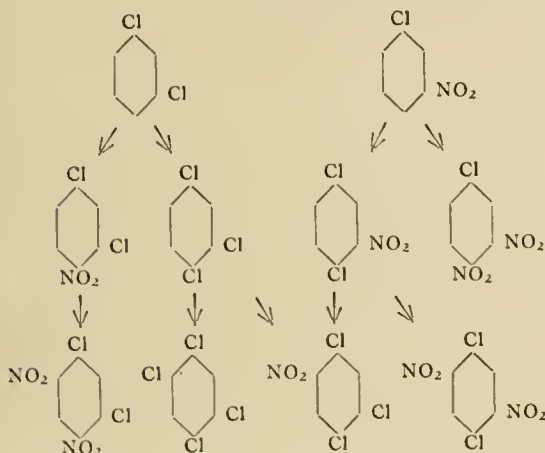
The smaller the yield of osazone precipitated by phenylhydrazine in the cold, the greater is the acidity of the solution. Attempts were made in the case of arabinose and rhamnose to isolate the acids formed during the oxidation. The simpler acids, formic and oxalic, were easily detected, but the more important keto-acids which were expected could not be isolated, although qualitative experiments leave little doubt as to their presence. Fischer's method (*Ber.*, 1902, xxxv., 3141) has been applied to the formation of arabinosone from arabinose, rhamnosone from rhamnose, and by using *o*-nitrobenzaldehyde, glucosazone and rhamnosazone may be made to yield the corresponding osones.

Radium emanations were found to have no influence on the oxidation of fructose. When the conditions were arranged so that change in the concentration of the solutions became impossible, the optical activity of the sugar remained constant.

35. "Studies in Chlorination. The Chlorination of the Isomeric Chloronitrobenzenes." By JULIUS BEREND COHEN and HUGH GARNER BENNETT.

In a recent paper by Cohen and Dakin (*Trans.*, 1904, lxxxv., 1274), attention was directed to the relation which was found to subsist between the position assumed by the third and fourth entrant chlorine atoms obtained by chlorinating *o*- and *p*-dichlorobenzenes and the six isomeric dichlorotoluenes, on the one hand, and those occupied by the two entrant nitro-groups on the other, and again by the fourth chlorine atom and nitro-group in the case of 1 : 2 : 4-trichlorobenzene and the six trichlorotoluenes.

The investigation has now been extended to the chlorination of *m*-dichlorobenzene and the mono- and di-chloronitrobenzenes. The results show remarkable conformity with the above rule, and no single exception has been recorded. It therefore follows that when the first two hydrogen atoms of benzene or toluene have been substituted by either two chlorine atoms or by one chlorine atom and one nitro-group, the positions occupied by subsequent chlorine atoms or nitro-groups are the same. The principal table of results is too long to reproduce, but that of the derivatives of *m*-dichloro- and *m*-chloronitrobenzenes will serve to illustrate the rule. The only secondary product recorded in this table is *p*-dichloro-*p*-dinitrobenzene. The remainder represent the sole products of each reaction:—



NOTICES OF BOOKS.

Conversations on Chemistry. Part I. General Chemistry.
By W. OSTWALD. Authorised Translation by ELIZABETH CATHERINE RAMSAY. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1905.

THE fundamental change which has come over the teaching of chemistry, not only in this country, is excellently illustrated in this work. This change is of such recent date that probably very few now engaged in teaching had the advantage of learning by the new method, though few indeed of them would dream of expecting their pupils to learn by the old method, the one advantage of which was that it was almost prohibitory to any but the most dogged, so that none but the fittest ever survived the initial stages in the study of the science. By reading this book teachers can obtain an excellent insight into the methods now adopted by a great master, who passes with brilliancy the test of giving elementary instruction, and many of them will no doubt be surprised to find how much they have still to learn. The setting of the lessons is excellent, the dialogues being supposed to take place between a teacher and a most perspicacious pupil, who, however, is not above falling into error and even forgetting what he has learnt. The book appears to be more especially suitable for use by the teacher only, though the author evidently contemplated its being put into the hands of students also. If this latter were the case, it seems likely that a certain artificiality in the cultivation of an enquiring mind by the student would result, whereas the teacher should be able to guide and train his pupils' minds so that, like the boy in the book, they would naturally ask the leading question and not catch hold of the trivialities which so often occur

first to children's minds, and the answers to which are often a source of considerable embarrassment to the teacher without leading to any advance in the knowledge of the student. The subjects treated in the book are the elementary conceptions regarding the properties of the elements oxygen, hydrogen, nitrogen, and carbon, the nature of mixtures, solutions, &c. The pupil who works through it would not be prepared to discuss the Atomic Theory or the laws of chemical combination, but would, if he were at all capable of benefitting by good teaching, be able to investigate the causes, conditions of occurrence, and details of any new phenomenon brought to his notice, to discover the essential points of any scientific problem, and to attack it in the right way. There can be no doubt which class of pupil is better equipped. The book is obviously the work of an enthusiastic teacher, and is interesting and amusing from beginning to end.

Kunstlicher Graphit. ("Artificial Graphite"). By FRANCIS A. J. FITZ-GERALD. Translated into German by Dr. MAX HUTH. Halle-a-S.: Wilhelm Knapp. 1904.

THE historical review with which this short monograph begins gives an interesting account of the investigations of the chief workers in this region. Despretz's, Berthelot's, and Moissan's researches are discussed in it, and in the case of the two latter copious quotations from their publications are included. The section on the preparation of artificial graphite is devoted chiefly to the description of the details of the Acheson method, which is treated with comparative fullness. The various patents taken out by Acheson seem to have been carefully abstracted, and the specification of that relating to the preparation of objects made of graphite, such as crucibles, &c., by the method in which the objects are first formed of amorphous carbon, which is then converted into graphite, is given at some length. The properties of graphite made by the Acheson method are also shortly discussed, and the consideration of some experiments dealing with the heating of carbon to high temperatures under great pressure, and other subjects connected with the preparation of graphite, conclude a useful monograph which, though so short as to be read through easily in about an hour, contains much valuable matter. A useful feature is the short abstract of the text given at the end of the book; this gives an excellent summary of our present knowledge of the subject.

Experimentelle Untersuchung von Gasen. ("The Experimental Study of Gases"). By Dr. MORRIS W. TRAVERS. F.R.S. Translated into German by Dr. TADEUSZ ESTREICHER. Braunschweig: Friedrich Vieweg und Sohn. 1905.

THE favourable reception accorded to the English edition of this work when it first appeared three years ago will no doubt be extended to the German translation. The author has carefully and thoroughly revised the original, and in some cases made considerable additions to it, when recent advances, either in the adoption of fresh methods or in the obtaining of fresh results, seemed to call for such a procedure, and the translator has contributed an excellent chapter on the latent heat of evaporation of liquefied gases. As the work now stands it provides a valuable text-book, describing the methods of the experimental study of gases, and the most important results hitherto obtained; in the case of the helium group of gases, upon which the author is particularly fitted to write authoritatively, much of the information has been brought together for the first time from the original papers. By a judicious selection of methods and results the author has succeeded in producing a most complete text-book, which yet does not exceed the limits of moderate size, and in which no point of importance is omitted.

CORRESPONDENCE.

URANIUM PRODUCTS.

To the Editor of the Chemical News.

SIR,—I would be very thankful to your readers if they will have the kindness to let me know the address of firms in England dealing or working in products containing uranium. I can offer these articles at very advantageous prices, and very soon.—I am, &c.,

S. KOHN.

Obermain-Anlage 8,
Frankfurt a. Main.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxi., No. 7, February 13, 1905.

Physical Constants of Pure Methane. Action of Solid Methane on Liquid Fluorine.—H. Moissan and M. Chavanne.—The authors prepare pure methane by the decomposition of aluminium carbide by cold water. They ascertain its density to be 0.555 as compared with air. The fusing-point is -184° . The colourless liquid obtained under these conditions boils at -164° under a pressure of 760. If a tube containing methane gas is drawn off to a fine point, and this broken off under liquid air, the methane solidifies in the point. If this point is broken off in contact with liquid fluorine at -187° a violent explosion takes place, showing that energetic chemical action persists even at these low temperatures.

A New Reaction of Aldehydes and Isomerism of their Oxides.—A. Conduché.—Compounds having the general formula $R-NH_2$ (ammonia, hydroxylamine, aniline, phenylhydrazine, &c.) give interesting condensation products when acted upon by aldehydes. When benzylic aldehyde is added to a dilute aqueous solution of hydroxylamine chlorohydrate and potassium cyanate in equimolecular proportions, a crystalline deposit is formed after some hours. This reaction is not peculiar to benzylic aldehyde, but derivatives may be obtained from anisic, salicylic, and metanitrobenzylic aldehydes, furfural, and cenanthol.

Action of Cyanhydric Acid on Epithylene.—M. Lespiau.—When epithylene, $\begin{array}{c} O \\ \diagup \quad \diagdown \\ CH_2-CH-CH_2OC_2H_5 \end{array}$, acts on cyanhydric acid, the nitrile $CH_2OC_2H_5-CHOH-CH_2-CN$ is obtained. The saponification of this compound by hydrochloric acid in presence of aqueous alcohol gives the ether salt, $CH_2OC_2H_5-CHOH-CH_2-CO_2C_2H_5$. The acid, $CH_2OC_2H_5-CHOH-CH_2-CO_2H$, or at least its potassium salt, can be obtained by dissolving the corresponding ether salt in alcohol, adding the theoretical quantity of potassium, and then evaporating in a dry vacuum. The author also prepares the nitrile $CH_2OC_2H_5-CHCl-CH_2-CN$.

Transformation of Amylo-cellulose into Starch.—Eugene Roux.—The retrogradation of starch is a reversible phenomenon between 0° and 150° . At the latter temperature, and in presence of excess of water, the amylo-cellulose becomes liquid and then undergoes a progressive retrogradation, which ultimately leads to a very simple form which iodine colours blue. In the dissolved state the products of this disintegration are capable of further retrograding, and producing once again the amylo-cellulose

from which they were derived. The ultimate products of this hydrolysis, of which no reversibility can be detected, is amylo-dextrine, amorphous dextrine, and finally ordinary glucose. By the incomplete disintegration of amylo-cellulose, artificial starches are obtained presenting the microscopic appearance of natural starches, which are turned blue by iodine and are only identified because they do not form a jelly in contact with boiling water and dissolve in alkalis without residue. Artificial starches, which are soluble or saccharifiable according to their method of preparation, should be considered as being complex mixtures still containing amylo-cellulose. Also, artificial starches derived from amylo-cellulose are identical with those which give the ordinary sediment most rapidly under normal conditions of temperature. Amylo-cellulose, natural or artificial starches, only differ chemically in the state of greater or less condensation of the same fundamental radicle.

Electrolysis of Organic Acids by Means of an Alternating Current.—André Brochet and Joseph Petit.—Already noticed.

Phosphorescence of Phosphorus.—E. Jungfleisch.—The author's experiments on the phosphorescence of phosphorus lead him to believe—(1) That the vaporisation of phosphorus at ordinary temperatures consists of such very minute particles of matter that they would be incapable of giving, by their combustion, luminous phenomena which would be comparable in intensity with phosphorescence; (2) the phosphorus, however, does pass into the surrounding gases, forming in contact with rarefied oxygen, or inert gases slightly impregnated with oxygen, an oxide of phosphorus which is much more volatile than phosphorus itself; (3) the luminous phenomena of phosphorescence result almost exclusively from the spontaneous combustion of the vapour of this phosphorus oxide coming in contact with oxygen; the variations in intensity depending chiefly on the circumstances under which this contact is effected.

MISCELLANEOUS.

Business Announcement.—The firm of H. E. Gerber and Co., Monterey, Mexico, is desirous of entering into business relations with manufacturers of caustic soda and bicarbonate of soda.

Congress of Chemistry and Pharmacy.—During the Universal and International Exhibition to be held this year at Liège, a Congress of Chemistry and Pharmacy will take place from July 27th to 30th, 1905, under the Patronage of the Belgian Government. Chemists and pharmacists from all countries are invited to attend and to join in the discussions of the various questions that will arise. The Congress will be divided into nine sections:—Section I. (General Chemistry, Physicochemistry); Section II. (Analytical, Commercial, Mineral Chemistry—including Metallurgy, Apparatus, and Instruments); Section III. (Organic Commercial Chemistry, Sugars, Fermentations, Tanning, Dyeing, &c.); Section IV. (Pharmaceutical Chemistry, Practical Pharmacy, Toxicology); Section V. (Chemistry of Foods); Section VI. (Agricultural Chemistry); Section VII. (Biological and Physiological Chemistry, Applications of Hygiene and Bacteriology); Section VIII. (Professional Matters, Deontology); Section IX. (History and Legislation). Papers are invited, and it is requested that they should be written or printed in both English, French, and German. The Congress will be under the Presidency of Prof. A. Gilkinet, of Liège, and there is a strong committee.

The Colloidal Metals of the Platinum Group.—C. Paal and C. Amberger.—We proceed in the same manner as M. Paal (*Verichte*, vol. xxxv., p. 219) by means of protalbic and lysalbic acids extracted by him from egg albumin (*Ibid.*, p. 2195); to an alkaline solution of

protalbate or lysalbate of sodium, we add PtCl_4 , for example; the reduction only takes place after heating for a considerable time, but in the cold it can be made to occur quickly by the addition of hydrate of hydrazine. If we then dialyse, we obtain, after evaporating in the cold, black brilliant friable plates, soluble in water, giving a black opaque solution. The addition of acetic acid gives a black flocculent precipitate containing platinum combined with the albuminoid acid, and which re-dissolves in alkaline solutions without leaving any residue. We obtain entirely similar results with palladium and protalbate of sodium, and again with lysalbate of sodium and tetrachloride of iridium; we then used sodium amalgam, or even a current of free hydrogen as the reducing agent. All these products act vigorously on peroxide of hydrogen, especially those having platinum or palladium as their base.—*Berichte*, vol. xxxvii., p. 124.

Some Halogen Compounds of Phosphorus and Platinum and their Derivatives.—A. Rosenheim and W. Lewenstamm.—The compound $\text{PtCl}_2 \cdot \text{PtCl}_2$, already prepared by Schutzenberger, is obtained by heating a mixture of 1 molecule of chloride of platinum, PtCl_2 , and trichloride of phosphorus for several hours to 130° in a sealed tube. If we put the PtCl_2 in suspension in CCl_2 , and then add PCl_3 in sufficient quantity, all the PtCl_2 is dissolved and the solution deposits bright yellow-coloured crystals having the formula $(\text{PtCl}_2)_2 \cdot \text{PtCl}_2$. This compound may be represented, according to Werner's theory, by $\left[\text{Pt} \left(\text{PCl}_3 \right)_2 \right]$, analogous to $\left[\text{Pt} \left(\text{NH}_3 \right)_2 \right]$. As for the compound $\text{PtCl}_2 \cdot \text{PCl}_3$, if we admit the correctness of the formula $\left(\text{Pt} \left(\text{PCl}_3 \right) \right)$, then the molecule would not be saturated. With the object of determining the molecular weights of compounds of this type, the authors have prepared some ethers. These were obtained easily by treating the chloride with alcohols. In this manner they prepared $\text{P}(\text{OC}_2\text{H}_5)_3 \cdot \text{PtCl}_2$ (large yellow prisms), $\text{P}(\text{OCH}_3)_3 \cdot \text{PtCl}_2$ (small well-formed needles). The determination of the molecular weights gave the formulae $\left[\text{Pt} \left(\text{PCl}_3 \right)_2 \right]$ and $\left(\text{Pt} \left(\text{PCl}_3 \right) \right)_2$. By the action of either chlorine or bromine on the ether $\left[\text{Pt} \left(\text{P}(\text{OC}_2\text{H}_5)_3 \right) \right]_2$, we obtain a phosphoric ether, $\left[\text{Pt} \left(\text{O} = \text{P}(\text{OC}_2\text{H}_5)_3 \right) \right]$. Bromine gives the chlorobromo-derivative, $\text{Pt} \left(\text{O} = \text{P}(\text{OC}_2\text{H}_5)_3 \right) \text{Br}$. These two compounds, which are respectively of a reddish yellow and a deep red colour, are well crystallised and are slightly soluble in benzene. Pentabromide of phosphorus, heated to about 250° with platinum black, gives a compound that the action of methylic alcohol transforms, not into $\text{Pt} \left(\text{P}(\text{OCH}_3)_3 \right)_2$, but into a compound consisting of $\text{O}_4\text{Pt} \left(\text{P}(\text{OCH}_3)_3 \right)_2$. The action of chlorine on the benzenic solutions of this new body gives the phosphoric ether, $\text{Pt} \left(\text{OP}(\text{OCH}_3)_3 \right)_2$. By adding triethylic phosphite to PtCl_2 in suspension in benzene, the authors obtained $\text{Pt} \left(\text{P}(\text{OC}_2\text{H}_5)_3 \right)_2$. By replacing the phosphorus ethers with the phosphoric ethers no reaction was observed.—*Zeit. Anorg. Chem.*, xxxvii., p. 394.

Indium.—C. Renz.—The product described by MM. Dennis and Geer (*Berichte*, vol. xxxvii., p. 664) has already been announced by the author (*Zeit. Anorg. Chem.*, vol. xxxvi., p. 107). A solution of InCl_3 in absolute alcohol treated with pyridine gives a white crystalline precipitate, or even, in dilute solution, white needles of $\text{InCl}_3 \cdot 3\text{C}_5\text{H}_5\text{N}$, slightly soluble in alcohol, almost insoluble in ether, fusible at 253° . Hydrate of indium is quite insoluble in diethyl amine in the presence of a little chlorhydrate, which enables

it to be separated from alumina. Oxide of indium calcined for a long time at a bright whitish-red heat in an iridium crucible does not fuse, but becomes converted into a bluish or greyish white powder containing a number of small cubical crystals. The author admits the existence of two modifications of In_2O_3 :—(1) The yellow amorphous oxide soluble in acids; (2) the crystalline oxide insoluble in acids. Metallic indium heated with selenium or tellurium unites vigorously, leaving black masses with a metallic lustre in the fracture; there is incandescence in the case of tellurium.—*Berichte*, vol. xxxvii., p. 2110.

MEETINGS FOR THE WEEK.

- MONDAY, 20th.—Society of Arts, 8. (Cantor Lecture). "Telephony," by Herbert Laws Webb, M.Inst.C.E.
TUESDAY, 21st.—Royal Institution, 5. "Engineering Problems," by Prof. W. E. Dalby, M.A., &c.
Society of Arts, 8. "West Country Screens and Round Lairs," by F. Bligh Bood, F.R.I.B.A.
WEDNESDAY, 22nd.—Society of Arts, 8. "The Present Aspect of the Fiscal Question," by Sir Charles Malcolm Kennedy, C.B.
THURSDAY, 23rd.—Royal Institution, 5. "The Reasonableness of Architecture," by Thos. G. Jackson, F.S.A., &c.
FRIDAY, 24th.—Royal Institution, 9. "A Pessimistic Current," by Sir Oliver Lodge, F.R.S., &c.
Physical, 8. (Pender Electrical Laboratory, University College). "Voltage Ratios of an Inverted Rotary Converter," by W. C. Clinton. "The Flux of Light from the Electric Arc with varying Power Supply," by G. B. Dyke. "Application of the Cymometer and the Determination of the Coefficient of Coupling of Oscillation Transformers," by Prof. J. A. Fleming. Exhibition of Cymometers and other Instruments.
SATURDAY, 25th.—Royal Institution, 3. "Electrical Properties of Radio-active Substances," by Prof. J. J. Thomson, F.R.S., &c.

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CHEMISTRY	J. E. MACKENZIE, Ph.D., D.Sc.
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MATHEMATICS	E. H. SMART, M.A.
BOTANY	A. B. RENDLE, M.A., D.Sc.
ZOOLOGY	H. W. UNTHANK, B.A., B.Sc.
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THE CHEMICAL NEWS.

VOL. XCI., No. 2365.

THE EFFECT OF TEMPERATURE ON WATER OF CRYSTALLISATION AS EVIDENCE FOR THE THEORY OF HYDRATES IN SOLUTION.

(TWELFTH COMMUNICATION).

By HARRY C. JONES and H. P. BASSETT.

IN the eleven preceding papers bearing on the theory of hydrates in solution, various lines of evidence have been furnished for the correctness of the theory. In recent papers* special stress has been laid upon the relation between water of crystallisation and molecular lowering of the freezing-point as evidence for the theory of hydrates to account for abnormally great freezing-point depressions, and, consequently, abnormally great osmotic pressures shown especially by concentrated solutions of electrolytes.

Judging from private correspondence, this view has already been fairly widely accepted.†

In a recent paper a preliminary calculation was made of the approximate composition of the hydrates formed by a number of substances of various dilutions (*Zeit. Phys. Chem.*, 1904, xlix., 385). These calculations were based upon the data then available. Since that time work has been in progress upon just this phase of the problem. The values of $\mu \infty$ for a number of substances as used in the paper just referred to, we find were too large. The true values have now been found as closely as possible, and the composition of the various hydrates formed by the different substances have been recalculated. The results will appear in the June number of the *American Chemical Journal*.

One very simple experiment, which shows that a substance in solution can combine with more water than it can bring with it out of solution, will be referred to. My attention was called to a number of colour reactions which point to the correctness of the theory of hydrates in aqueous solutions by Dr. Lewis, of Harvard. Some of these will be referred to in a review of my entire work in this field which will soon appear in the *Journal de Chimie Physique*. A modification of one of these experiments is the following:—Into a concentrated solution of cobalt chloride or nitrate introduce a fairly large quantity of crystallised calcium chloride. Shake the solution for a time and it will gradually become blue, showing that the cobalt chloride has been dehydrated by the calcium chloride. Since this cannot be accounted for on the ground of the formation of a double chloride, or by the driving back of the dissociation of one salt by adding a common ion, it shows that calcium chloride in solution can combine with more than 6 molecules of water. In a word, that a salt in solution can combine with more water than it can bring with it out of solution as water of crystallisation.

The main object of this paper is to call attention to a new line of evidence, which it seems to us bears very directly on the theory of hydrates in aqueous solution.

* *Am. Chem. Journ.*, 1904, xxxi., 303; *Zeit. Phys. Chem.*, 1904, xlix., 385; *Berichte*, 1904, xxxvii., 1511; *Journal de Chimie Physique* (in the near future).

† In a recent paper (*Ber.*, xxxvii., 3036), Hr. W. Biltz would argue against the theory by reciting a number of facts known to everyone but the merest beginner in physical chemistry. The one or two points in his paper that might be taken seriously had already been discussed in Jones's own papers. After entering a field which had been opened up systematically for the first time in this laboratory, and in which two papers had already been published, in our opinion he failed entirely to see the significance of even the results that he himself had obtained.

Salt.	Water of crystallisation.	Temperature of crystallisation.
Na_2CO_3	$7\text{H}_2\text{O}$	Warm saturated solution.
Na_2CO_3	$10\frac{1}{2}\text{H}_2\text{O}$	Ordinary temperatures.
LiCl	$2\frac{1}{2}\text{H}_2\text{O}$	+12.5°.
LiCl	$3\text{H}_2\text{O}$	-15°.
CaCl_2	H_2O	At the temperature of crystallisation it is lower and lower.
CaCl_2	$2\frac{1}{2}\text{H}_2\text{O}$	
CaCl_2	$4\frac{1}{2}\text{H}_2\text{O}$	
CaCl_2	$6\frac{1}{2}\text{H}_2\text{O}$	
$\text{Sr}(\text{NO}_3)_2$	Anhydrous	Above +16.8°.
$\text{Sr}(\text{NO}_3)_2$	$4\text{H}_2\text{O}$	Below +16.8°.
MgCl_2	$6\frac{1}{2}\text{H}_2\text{O}$	Elevated temperatures.
MgCl_2	$8\text{H}_2\text{O}$	Above +20°.
MgCl_2	$10\text{H}_2\text{O}$	+20°.
MgCl_2	$12\text{H}_2\text{O}$	-10° to -12°.
MgBr_2	$4\text{H}_2\text{O}$	+11.5° to +12.5°.
MgBr_2	$6\frac{1}{2}\text{H}_2\text{O}$	
MgBr_2	$10\text{H}_2\text{O}$	
$\text{Mg}(\text{NO}_3)_2$	$2\text{H}_2\text{O}$	Elevated temperatures.
$\text{Mg}(\text{NO}_3)_2$	$6\text{H}_2\text{O}$	+18°.
$\text{Mg}(\text{NO}_3)_2$	$9\text{H}_2\text{O}$	-17°.
ZnCl_2	H_2O	Elevated temperatures.
ZnCl_2	$3\text{H}_2\text{O}$	-21°.
$\text{Zn}(\text{NO}_3)_2$	$3\text{H}_2\text{O}$	+36°.
$\text{Zn}(\text{NO}_3)_2$	$6\text{H}_2\text{O}$	From concentrated solution
$\text{Zn}(\text{NO}_3)_2$	$9\text{H}_2\text{O}$	-18°.
$\text{Cd}(\text{NO}_3)_2$	$4\text{H}_2\text{O}$	Ordinary temperatures.
$\text{Cd}(\text{NO}_3)_2$	$9\text{H}_2\text{O}$	+10° to -16°.
MnCl_2	$2\text{H}_2\text{O}$	+20°.
MnCl_2	$4\text{H}_2\text{O}$	+15°.
MnCl_2	$6\frac{1}{2}\text{H}_2\text{O}$	-21°.
MnCl_2	$11\text{H}_2\text{O}$	From -21° to -37°.
MnCl_2	$12\text{H}_2\text{O}$	-48°.
MnI_2	$4\text{H}_2\text{O}$	0° to -27°.
MnI_2	$6\text{H}_2\text{O}$	-5°.
MnI_2	$9\text{H}_2\text{O}$	-20°.
MnSO_4	$3\text{H}_2\text{O}$	+25° to +31°, as a crust.
MnSO_4	$4\text{H}_2\text{O}$	+25° to +31°.
MnSO_4	$5\text{H}_2\text{O}$	+15° to +20°.
MnSO_4	$7\text{H}_2\text{O}$	0° or below +6°.
$\text{Ni}(\text{NO}_3)_2$	$3\text{H}_2\text{O}$	+58° and above.
$\text{Ni}(\text{NO}_3)_2$	$6\text{H}_2\text{O}$	-16°.
$\text{Ni}(\text{NO}_3)_2$	$9\text{H}_2\text{O}$	-27°.
$\text{Co}(\text{NO}_3)_2$	$3\text{H}_2\text{O}$	+56° to +91°.
$\text{Co}(\text{NO}_3)_2$	$6\text{H}_2\text{O}$	-22° to +56°.
$\text{Co}(\text{NO}_3)_2$	$9\text{H}_2\text{O}$	-29° to -22°.
$\text{Cu}(\text{NO}_3)_2$	$3\text{H}_2\text{O}$	At ordinary temperatures.
$\text{Cu}(\text{NO}_3)_2$	$6\text{H}_2\text{O}$	About 0° to -10°.
$\text{Cu}(\text{NO}_3)_2$	$9\text{H}_2\text{O}$	-20° to -24°.
AlCl_3	$6\text{H}_2\text{O}$	+2° to +20°.
AlCl_3	$9\text{H}_2\text{O}$	-8° to +2°.
AlBr_3	$6\text{H}_2\text{O}$	Ordinary temperatures.
AlBr_3	$15\text{H}_2\text{O}$	-10° to -18°.
AlI_3	$6\text{H}_2\text{O}$	Ordinary temperatures.
AlI_3	$15\text{H}_2\text{O}$	-18°.
FeCl_3	Anhydrous	+80° and above.
FeCl_3	$2\text{H}_2\text{O}$	+60° to +80°.
FeCl_3	$2\frac{1}{2}\text{H}_2\text{O}$	+40° to +60°.
FeCl_3	$3\frac{1}{2}\text{H}_2\text{O}$	+20°.
FeCl_3	$6\text{H}_2\text{O}$	+20° to -16°.

These hydrates are not stable compounds, especially at elevated temperatures. This is shown by the fact that most of the water can readily be driven off from solutions of the various salts at the boiling-points of these solutions. The lower the temperature, however, the more stable will these hydrates become. This being the case, we would

expect that a salt would be able to bring out of solution more water, as water of crystallisation, the lower the temperature at which the crystals were formed.

On examining the literature with reference to this point, we find a fairly large amount of evidence available, and all pointing in the same direction. There exist already on record a large number of examples of salts that crystallise with varying amounts of water. A few are given above to bring out the apparently general relation that the number of molecules of water of crystallisation is greater the lower the temperature at which the salt is crystallised.

There is a much larger number of cases on record where the water of crystallisation varies with the temperature, but in many cases the temperatures at which the salts were crystallised are not given at all, or are given only approximately.

The above examples, however, suffice to show the general character of the relation between water of crystallisation and the temperature at which the salt is crystallised.

It is, of course, not a new idea that the lower the temperature the larger the number of molecules of water of crystallisation. It must be repeated that the fact is brought out here on account of its important bearing on the theory of hydrates in aqueous solutions which has recently been advocated strongly by Jones.

It might be thought that such facts as those given above are against the relations established by Jones and Getman between water of crystallisation and lowering of the freezing-point (*Amer. Chem. Journ.*, 1904, xxxi., 303; *Zeit. Phys. Chem.*, 1904, xlix., 385; *CHEMICAL NEWS*, lxxix., 157). An examination of those relations, however, will show that this is not the case. The amounts of water of crystallisation, as given by Jones and Getman for the various salts, are the quantities with which the various salts crystallise under as nearly comparable conditions as possible. These are really the hydrates that are the most stable at ordinary temperatures, and are, therefore, generally given in the literature and text-books as the amounts of water with which the various salts crystallise.

We have taken up in this laboratory a study of the relation between water of crystallisation in general and the temperature of crystallisation, and work is now in progress on this problem. We propose to study in the near future as many salts as possible in this connection.

As we have seen, there are, however, already on record a sufficient number of well-established cases to bring out the general nature of the relation.

We consider the above line of evidence as of very considerable importance in connection with the theory of hydrates proposed by Jones (*Am. Chem. Journ.*, 1900, xxiii., 103) to account for the abnormal freezing-point depressions produced by concentrated solutions of electrolytes and some non-electrolytes. The importance of this theory of concentrated solutions, as has been pointed out, is in connection with the failure of the gas laws to apply to concentrated solutions. The chief cause of this failure is to be found in the fact that concentrated solutions are in reality much more concentrated than we would expect from the amount of salt contained in them. A part of the water is combined with the dissolved substance, and this part no longer acts as solvent. The total amount of combined water, temperature being constant, is greater the more concentrated the solution.

Chemical Laboratory,
Johns Hopkins University, Baltimore, U.S.A.,
February, 1905.

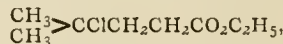
New Work.—Next week the Walter Scott Publishing Co., Ltd., will publish the absorbing work, "Science and Hypothesis," by Monsieur Poincaré, the famous French mathematician and savant. This work is prefaced with an Introduction from the pen of Joseph Larmor, M.A., D.Sc., Secretary of the Royal Society.

A CORRECTION.*

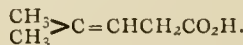
By WILLIAM A. NOYES and HOWARD W. DOUGHTY.†

SOME time ago one of us effected the synthesis of what were supposed to be β,β -dimethyladipic acid and α,β,β -trimethyladipic acid (*Journ. Am. Chem. Soc.*, 1901, xxiii., 392). Recently Blanc has prepared the former acid by a method which seems not likely to involve a molecular rearrangement, but has found the properties of his acid radically different from those of ours (*Comptes Rendus*, cxxxix., 800). He has been kind enough to call our attention to the difference, and to suggest that the formation of our acid may have been accompanied by a molecular rearrangement.

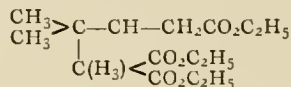
On examination of the literature, the close agreement between the melting-point of the acid which one of us has described as β,β -dimethyladipic acid and the melting-point of β -isopropylglutaric acid (Howles, Thorpe, and Udall, *Journ. Chem. Soc.*, lxxvii., 942), and also the agreement between the melting-point of the acid which was described as α,β,β -trimethyladipic acid and that of *cis*- α -methyl- β -isopropylglutaric acid was noticed (Howles, Thorpe, and Udall, *Journ. Chem. Soc.*, lxxvii., 946). The β -isopropylglutaric acid might have been formed in our synthesis as follows:—The chlorisocaproic ester,—



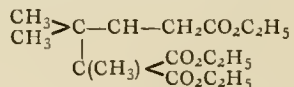
loses hydrochloric acid on boiling with the sodium malonic ester, giving pyroterebic ester,—



The terebic ester might then add the sodium malonic ester, with the formation of the sodium derivative of the ester,—



This ester, on saponification and loss of carbon dioxide, would give β -isopropylglutaric acid. On the other hand, if this ester were treated with sodium ethylate and methyl iodide, as was done in preparing the supposed α,β,β -trimethyladipic acid, it would give the ester,—



This, on saponification and loss of carbon dioxide, would give α -methyl- β -isopropylglutaric acid.

A sample of the supposed β,β -dimethyladipic acid had fortunately been saved from the previous investigation, and we have now prepared from it the anhydride by treating it with acetyl chloride, as described by Howles, Thorpe, and Udall.

The anhydride proved to be an oil, agreeing in this with the anhydride of β -isopropylglutaric acid, while our acid, if it were in reality dimethyladipic acid, should give no anhydride.

Our first attempt to prepare the anilic acid gave a compound which decomposed with charring at 250°. This may possibly have been the dianilide or the anil, as the material was over-heated at one point in the preparation. On repeating the experiment, by mixing a solution of the anhydride in benzene with aniline, the aniline salt of the anilic acid was obtained. After crystallisation this melts at 124°. The analyses gave 8.14 and 8.16 per cent of nitrogen; calculated for $\text{C}_{20}\text{H}_{26}\text{O}_3\text{N}_2$, 8.20 per cent. The

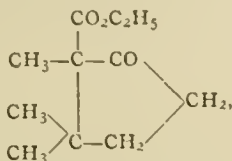
* From the *Journal of the American Chemical Society*, March, 1905.

† The work here described was carried out with the aid of the Carnegie Institution.

anilic acid melted at 121° , as given by Howles, Thorpe, and Udall (*loc. cit.*).

There is no doubt, therefore, that the acids which one of us formerly described as dimethyl- and trimethyladipic acids were in reality β -isopropylglutaric acid and α -methyl- β -isopropylglutaric acid. The acid which Blanc has described as β , β -dimethyladipic acid (*loc. cit.*) is, doubtless, what he supposes it to be, while the pure α , β , β -trimethyladipic acid is still unknown.

It may be added that, after the work published four years ago had been completed, a year or more was spent in the endeavour to secure a synthesis of a derivative of camphor from the acid, which was then supposed to be the trimethyladipic acid. The synthesis is tedious, but about 5 grms. of the pure acid were finally obtained. This was converted into the ethyl ester, and an attempt was made to condense this to a derivative of trimethylcyclopentanone,—



by heating it with sodium wire and toluene. This was unsuccessful, as was also an attempt to condense the ethyl ester of the supposed dimethyladipic acid in a similar manner. The cause of the failure is now apparent, but as no positive results were obtained, an account of that work has never been published.

At the time the possibility that the supposed di-methyl adipic acid might be, in reality, isopropylglutaric acid was more than once considered, but the suspicion was always dismissed because of the successful synthesis of trimethylcyclopentanone* which had been effected with an acid prepared in a similar manner. It might seem, on a superficial examination, that the facts now given throw a doubt on the validity of that synthesis. On examining the account of the work it will be seen, however, that in that synthesis bromoisocaproic ester was used instead of the chlorisocaproic ester employed in the later work; further, that the trimethyladipic acid used was not purified, but was mixed with lime and distilled in its crude form. In the subsequent purification of the ketone and its oxime the products derived from the methylisopropylglutaric acid, which was doubtless present, were separated, and the pure oxime of trimethylcyclopentanone was obtained. The comparison of the oxime with that obtained from camphor, and especially the fact that mixtures of the two had the same melting-point as either alone, placed the fact of their identity beyond question.

It seems probable, too, that the dimethylcyanocarboxyethylcyclopentanone (*Am. Chem. Journ.*, xxii., 260) and the dimethyldicarboxyethylcyclopentanone (*Journ. Am. Chem. Soc.*, xxiii., 326), described by one of us, have the structure which has been assigned to them. It is difficult otherwise to account for the products formed by their saponification.

Johos Hopkins University, Baltimore.
Bureau of Standards, Washington.

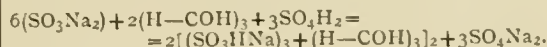
* *Am. Chem. Journ.*, xxiii., 128; *Ber.*, 1900, xxxiii., 54. In a paper published in 1903 (*Proc. Chem. Soc.*, xix., 61; *CHEMICAL NEWS*, lxxxvii., 140), W. H. Perkin and J. F. Thorpe stated, in describing their synthesis of the α - and β -campholytic acids, that their synthesis was the first of a compound containing the trimethylcyclopentane ring which is characteristic of camphor. I at once wrote to Professor Perkin reminding him of the synthesis which I had described more than three years before. He acknowledged my claim to priority, and promised to correct the statement in his full paper, which was to appear later. When the full account of his work was published (*Journ. Chem. Soc.*, 1904, lxxxv., 128) the erroneous statement referred to was omitted, but no correction of the earlier statement was made. After further correspondence, Professor Perkin has agreed that I shall publish the correction myself.—W. A. NOYES.

THE ESTIMATION OF FORMIC ALDEHYDE AND ITS POLYMERS.

By A. SEYEWETZ and M. GIBELLO.

ONE of us has shown (Lumière and Seyewetz, *Moniteur Scientifique*, February, 1903) that, on adding titrated sulphuric acid to a solution of trioxymethylene in sulphite of soda in the presence of phenolphthalein, it is necessary, to obtain the decolouration of the phenolphthalein, to use a quantity of titrated acid proportional to the amount of trioxymethylene dissolved in the alkaline sulphite. G. Lemme (*Chemiker Zeitung*, 1903, No. 74) has confirmed these results by titrations of formic aldehyde with normal sulphuric acid in the presence of sulphite of soda. He finds that formic aldehyde added to sulphite of soda decomposes the latter into bisulphite of soda, with which it combines, and into caustic soda, which is set free, and that this alkali can be estimated by the addition of titrated sulphuric acid to the mixture of sulphite of soda and formic aldehyde.

We have observed that no reaction appears to take place in the cold between formic aldehyde and sulphite of soda alone, but that the addition of sulphuric acid by decomposing the sulphite of soda into bisulphite and sulphate of soda causes the production of the bisulphitic compound. The bisulphite of soda being absorbed instantly by the aldehydic compound, and the bisulphitic compound being neutral to phenolphthalein, the titrated sulphuric acid does not exercise its decolourising action on the phenolphthalein except after having liberated a quantity of bisulphite sufficient to absorb the whole of the formic aldehyde. This reaction can be expressed by the following equation:—



We have applied this reaction to the rapid titration of the polymers of formic aldehyde, such as trioxymethylene, which are not soluble in water, but dissolve easily in sulphite of soda, and to other new polymers that we shall describe later on.

To carry out this method of titration, we prepare a solution of anhydrous sulphite of soda at about 20 per cent, and take, say, 20 c.c., to which we add a drop of an alcoholic solution of phenolphthalein at 2 per 1000. We determine first of all the amount of titrated acid necessary to neutralise the alkaline reaction of the sulphite by adding titrated acid until the phenolphthalein is just decoloured. This figure having been determined once for all, we dissolve in the 20 c.c. of the solution of sulphite from 0.5 to 0.7 gm. of trioxymethylene. Immediately the red colour of the phenolphthalein reappears, by reason of the absorption by the dissolved trioxymethylene, of the small quantity of bisulphite of soda formed in the sulphite by the addition of titrated acid, and which communicates its acid reaction to the solution.

We have found that an excess of sulphite is necessary for the bisulphitic combination to take place instantly, and for the titration to give absolutely constant figures. It is better also to add only the amount of phenolphthalein just necessary to obtain a distinct colouration.

By making a series of titrations on a sample of trioxymethylene that had been air-dried for a long time, after a large number of estimations on varying dissolved amounts, we obtained constant results corresponding to 91 per cent of CH_2O . After keeping this sample of trioxymethylene for five days in a vacuum over sulphuric acid the results of the titrations did not vary noticeably. When working under similar conditions with a solution of commercial formic aldehyde, we found that it contained 37.5 grms. per cent of CH_2O .

This method has enabled us to estimate formic aldehyde in very dilute solutions with an approximation not obtainable by other methods. In a solution containing 1 gm. of the above-mentioned formic aldehyde in 1 litre of water,

that is to say, 0.037 grm. of CH_2O in 1 litre of water, we found by titration 0.0375 grm. and 0.0373 grm.

We have compared the results given by this method with those given by Legler's method (*Berichte*, vol. xvi., p. 1333), modified by Lösekann (*Berichte*, vol. xxii., p. 1565), which according to the comparative examination of the different methods of titrating formic aldehyde, published by Craig (*Am. Chem. Soc.*, vol. xxiii., p. 638; *Moniteur Scientifique*, 1902, p. 670), is the one giving the most constant results.

It consists in heating trioxymethylene for one hour on a boiling water-bath with a solution of normal ammonia in a hermetically stoppered flask. The trioxymethylene is transformed into hexamethylenetetramine, and from the titration of the excess of ammonia in the presence of methyl-orange or litmus we deduce the percentage of CH_2O , remembering in the former case the mono-basicity of hexamethylenetetramine to methyl-orange. The figures obtained, according to Craig, by Legler's method for the titration of a well dried commercial trioxymethylene, are between 91 and 92 per cent, and for a commercial formic aldehyde between 37 and 38 per cent.

On repeating these estimations on trioxymethylene, and also on the commercial formic aldehyde we titrated above, we obtained by Legler's method figures quite comparable with those given by Craig, and consequently very close to those we found by means of our own method.

The Legler-Lösekann method is rather a delicate one to do, on account of the heating in a closed vessel. The results obtained may be easily vitiated by the loss of ammonia that the normal solution may undergo. The use of methyl-orange or litmus as an indicator is not convenient, as with these reagents there is only a limited period of sensitiveness; and again, we can only detect the exact point of saturation after a certain amount of practice.

The method we have proposed seems to us to be much more easy of execution. It can be used in the cold and only requires a titrated solution of acid of the strength of which there is no fear of alteration; further, it gives remarkably constant results, even with very dilute solutions. —*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 11.

THE ESTIMATION OF MANGANESE BY THE PERSULPHATE METHOD.

By H. SUDERT.

THE work of G. von Knorre on the determination of manganese in the presence of iron (*Zeit. f. Angew. Chem.*, 1903, No. 38) caused me to take up this subject. I therefore made a series of determinations of manganese in the presence of iron by precipitating the manganese by persulphate of ammonium, as recommended by Knorre. I found, first of all, that Knorre's method (transformation of the manganese into persulphate, decomposition of this salt by boiling, solution of the peroxide formed in peroxide of hydrogen, and back titration with permanganate of the excess of this reagent) gave excellent results. I then set to work to simplify it and to render it applicable to rapid determinations. We might in this manner devise a method of analysis enabling us to obtain exact results with rapidity without the inconveniences of the volumetric methods of Hampe and Volhard. It is in this respect that I look upon as defective the long and tedious solubilisation with sulphuric acid treated with nitric acid proposed by Knorre, the filtration which follows this operation, and the neutralisation of the excess of acid by ammonia. My experiments have enabled me to simplify these points in the following manner:—

Knorre states that the presence of nitrates has no deleterious influence; I therefore dissolved the scraps of iron to be analysed in nitric acid. In this way the solution is more rapid and more certain than in sulphuric acid, for we can make quite certain of the end of the operation,

which is not always easy when we use sulphuric acid. Further, we can omit the filtration, the solution being already perfectly limpid, and we need only dilute it with a large quantity of water.

We can also do without the neutralisation with ammonia; parallel experiments have shown me that nitric acid in excess does not interfere if we observe the following conditions:—According to Knorre's instructions, we then add persulphate of ammonium and sulphuric acid, and boil briskly to transform the persulphate of manganese, and decompose the excess of persulphate of ammonium. We add to the liquid, cooled to the ordinary temperature, a known quantity of peroxide of hydrogen of known strength; the peroxide of manganese dissolves easily, and we titrate the excess of peroxide of hydrogen with permanganate.

Ledebur has described one of Knorre's methods in his "Leitfaden für Eisenhüttenlaboratorien"; it is the one in which we filter the precipitate of peroxide and then dissolve it in ferrous sulphate. On this subject he says that the precipitate is poorer in oxygen in proportion as a larger quantity of carburised compounds of iron have passed into solution.

I have not observed the truth of this remark with irons of which the proportion of carbon reached 1.2 per cent, but I have always obtained good results when operating as I have just described. But we have, further, the advantage over Knorre's method, described by Ledebur, of doing away with the tedious filtration of the peroxide of manganese. The graphite that separates out, however, has an interfering action, and should be separated by filtration. The analysis of a sample of ferro-manganese at 82 per cent of manganese also showed the advantage of solution in nitric acid; in this way the whole of the manganese went into solution, which is not possible by the sulphuric acid treatment.

We have made the following estimation by the process just described; we dissolved in 50 c.c. of boiling nitric acid 4 grms. of a sample of iron containing, according to gravimetric analysis, 0.60 per cent of manganese, estimated in the form of MnS , and 0.66 per cent of carbon. The density of the acid was 1.2, and the operation was carried out in an Erlenmeyer flask of 1 litre capacity. The liquid was diluted, without previous filtration, with 400 c.c. of water, then treated with 40 c.c. of sulphuric acid (density = 1.18) and 50 c.c. of a solution of persulphate at 120 grms. to the litre. After boiling briskly for half-an-hour, the contents of the flask were cooled, and we added to the solution 15 c.c. of peroxide of hydrogen of which 10 c.c. were equal to 9.4 c.c. of the solution of permanganate. The equivalence of these solutions should be measured every day, as the strength of the peroxide of hydrogen varies with great rapidity.

After complete solution of the peroxide of manganese, we used 5.2 c.c. of permanganate to neutralise the excess of the peroxide of hydrogen. One c.c. of KMnO_4 is equal to 0.00577 grm. of Fe. The strength had been already established by means of pure double sulphate of iron and ammonium; the value in manganese is therefore:—

$$0.00577 \times \frac{55}{112} = 0.00577 \times 0.491 = 0.00283,$$

15 c.c. of H_2O_2 = 14.1 c.c. KMnO_4 . The excess of H_2O_2 = 5.2 c.c. KMnO_4 . The MnO_2 was equal to 14.1 - 5.2 = 8.9 c.c. of permanganate. Thus the iron contained:—

$$\frac{8.9 \times 0.00283 \times 100}{4} = 0.62 \text{ per cent Mn.}$$

Knorre's method has the following advantages over that of Hampe and Volhard.

1. We avoid the disagreeable evolution of chlorine met with in Hampe's method.
2. The whole analysis is effected in the same vessel; thus we do away with the errors accompanying filtration transference, &c.

We have made the same determinations on a series of samples of iron, and we give below some of the results:—

Carbon. Per cent.	Manganese.	
	Estimated as MnS.	Estimated as persulphate.
0.73	0.59	0.61
0.75	0.62	0.63
0.40	0.97	0.98
0.40	0.84	0.88
0.90	1.42	1.45
0.07	0.05	0.04
0.06	0.27	0.28
1.14	0.51	0.53
0.73	0.58	0.62
0.62	0.62	0.65
0.71	0.61	0.64
0.40	0.81	0.83
0.74	0.40	0.43
0.27	0.85	0.88
0.11	0.48	0.50
0.10	0.50	0.51
0.15	0.46	0.48
0.14	0.47	0.49
1.20	0.20	0.20

3. The final point of the titration is distinct and easy to see, which is not always the case when we use Volhard's method.

4. The analyses are rapid, and do not require very close attention.

Thus the method is to be recommended commercially. One exception must be made if the iron contains tungsten; analyses made up to the present have not given good results in such cases, but we are pursuing the matter.—*Zeitschrift für Angewandte Chemie*, 1904, p. 422.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING FEBRUARY 28TH, 1905.

By SIR WILLIAM CROOKES, F.R.S.,
and
SIR JAMES DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, March 9th, 1905.

SIR,—We submit herewith, at the request of the Metropolitan Water Board, the results of our analyses of the 216 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the Metropolitan Water Board taking their supplies from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Feb. 1st to Feb. 28th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 216 samples examined by us during the month, all were clear, bright, and well filtered.

The deficit of rain recorded last month still continues; only 0.39 inch was measured at Oxford during the month of February. The average fall is 1.80 inches, so we have

a further deficit of 1.41 inches, which, if added to the previous one for January, makes a total deficit of 2.71 inches, or 69.8 per cent on the thirty-five years' average.

Our bacteriological examinations of 378 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 473 others from special wells, standpipes, &c., making 851 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 24 samples) ..	220
New River, filtered (mean of 70 samples) ..	8
Thames, unfiltered (mean of 24 samples) ..	1392
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 189 samples) ..	13
Ditto ditto highest	185
Ditto ditto lowest	0
River Lea, unfiltered (mean of 24 samples) ..	174
River Lea, from the East London District clear-water wells (mean of 24 samples) ..	27
Kent District, from the wells at Deptford (mean of 23 samples) ..	30

Of the 306 daily samples taken from the general wells of the Metropolitan Water Board, twenty-seven samples, or 8.8 per cent, were sterile. Eight samples, or 2.6 per cent, contained more than 100 microbes, and of these three samples contained more than 150 microbes per c.c. The eight excess samples contained an average of 138 microbes per c.c. In January fifteen excess samples contained an average of 159 microbes per c.c.

From the above results it will be seen that the quality of the water supplied to London during the month of February was excellent, and better than we are accustomed to have at this time of year. No doubt this is due, in great measure, to the deficiency in the rainfall during the past seven months.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

JAMES DEWAR.

THE IMPORTANCE OF ACCURATE MEASUREMENTS AT VERY LOW TEMPERATURES.*

By Dr. H. KAMERLINGH ONNES.

THE territory of low temperatures has always tempted the experimenters. Boyle considered the difficulties he met with at the threshold of this study to be greater than those in any other branch; they still increase as we approach the greatest imaginable cold. The arctic regions in physics incite the experimenter, as the extreme north and south incite the discoverer. Yet both with respect to the difficulty and to the importance which accompanies the attainment of the object there is a great difference between the efforts of these two. There is no doubt that, with still greater exertion and with increase of means, the geographical poles can be reached, and the nearer they are approached the less significant becomes the further advance. The greatest imaginable cold, however, lies for ever at an infinite distance, while at every step forward the importance of the attainable new scientific data increases.

When people first began to put the questions how they might best push their way to the North Pole and how they might reach the lowest temperatures, the points of agreement between the two subjects were still very numerous. And with pride we mention the fact that, as the Dutch

* Address delivered in commemoration of the 329th Anniversary of the University of Leiden. From *Communications from the Physical Laboratory at the University of Leiden*, Suppl. No. 9 to No. 85—96.

were the pioneers in the North Polar voyages, it was our compatriot van Marum who took the initiative step on the path which led to the production of the lowest temperatures in the last century.

It has been represented as if van Marum found accidentally that ammonia could be liquefied, and that he did not understand the significance of his discovery. As Bosscha has demonstrated in his splendid Address, this view was false.

Van Marum had learned to show very clearly the difference between the vapour tensions in substances of different volatility by placing several barometer tubes next to each other in a mercury vessel and introducing into each of them a small quantity of liquid above the mercury. While at ordinary temperature ether presses the mercury column down in the barometer to about half the normal height of 76 c.m.—in other words, shows a *vapour pressure* of half an atmosphere—the vapour pressure of water amounts to only 1.5 c.m. Ether need only be heated to 35° C., whereas water must be heated to 100° C. in order to raise the vapour pressure to 1 atmosphere and to make it boil.

If the space above the mercury is enlarged or diminished by moving the barometer tube up or down in the mercury vessel, the pressure remains unaltered and the liquid passes over into vapour or *vice versa*. If only so small a quantity of ether is admitted into the tube that there is no liquid above the mercury, but only evaporated ether, then this follows the law of Boyle, *i.e.*, if we move the tube up and down, the pressure varies directly proportionately to the density, in the same way as when air or another gaseous substance, ammonia gas for instance, lies on the mercury.

In order to compare the compressibility of ammonia gas with that of air under a higher pressure than 1 atmosphere, van Marum placed a mercury bath with two barometer tubes—one with air the other with ammonia gas—above the mercury, under a bell-jar into which he compressed air. He soon perceived that the density of ammonia increased a little more rapidly than the pressure he applied to it, and thus detected deviations from the law of Boyle. The appliances of those days did not permit him to carry compression to any great extent; although fortunately far enough. When the pressure was raised to 3 atmospheres—the ammonia being moist—a clear liquid separated on the mercury, which evaporated again on increasing the volume, while the pressure remained almost unvaried.

Thus, in the main, ammonia behaved like ether. The difference between the two substances is that, while at ordinary temperature the vapour pressure of ether is lower, that of ammonia is much higher than 1 atmosphere—in other words, that at ordinary temperature liquid ether is below, while liquid ammonia is far above its melting-point.

Between the experiment of van Marum, who first saw the easily liquefiable ammonia as a liquid, and those of Cailletet and Pictet, who first saw oxygen liquefied, lies a long way.

Van Marum had reduced the volume until it no longer could contain the whole quantity of substance at the temperature of the tube as a vapour; Faraday, however, forced a surplus of substance into a limited space. While decomposing hydrate of chlorine in one branch of a sealed glass tube, in the other he saw the generated chlorine liquefy under its own generation pressure.

Thus Faraday had found the way for the liquefaction of several other gases. This succeeded very well in the case of sulphur dioxide; its boiling-point lies at -10° C., and hence it liquefies when cooled with a mixture of ice and salt in an open vessel.

Living at the much lower temperature of -52° C., once observed during Nansen's polar expedition, we should not call sulphur dioxide a gas but a volatile liquid. We should have to heat it in order to make it boil at -10° C. Under the same circumstances ether would be considered to possess very little volatility; and ammonia to be as volatile as ether at the summer temperature of our climate. Other gases, however, might also be liquefied at that low temperature, but then only under a fairly high pressure, as, for

instance, carbon dioxide, which Faraday could keep as a liquid only in his strongest tubes, and even these often burst with a loud report. In order to reach the boiling point of this substance the cooling must be carried much further.

The means for further refrigeration could be produced, as Humphry Davy remarked, by the liquid gases themselves. Water, when run off from a steam-boiler in which it is heated above its boiling point to an excess of pressure above the atmospheric pressure, cools by vaporisation until the vapour pressure has become equal to the atmospheric; in the same way gas kept liquefied under an excess of pressure must cool down to its boiling point when freed from that excess of pressure.

Thilorier has applied this method of procedure. The bold idea occurred to him to use, instead of Faraday's narrow glass tubes, heavy wrought iron apparatus for the liquefaction of carbon dioxide. In this way he could produce such a large quantity of liquid carbon dioxide that, as it suddenly escaped from his reservoir into the atmosphere by running off through a stopcock, a portion could be collected as carbon dioxide-snow at -78° C., although the greater part of it passed over into vapour. Still lower temperatures were obtained by causing solid carbon dioxide to evaporate *in vacuo*.

The great significance of this advance towards the production of low temperatures made by Thilorier, appeared best when Faraday was again seized with an idea, which had formerly absorbed all his best powers, to bring all gaseous substances into the liquid state of aggregation.

With six of them, among which were oxygen, nitrogen, and hydrogen, all his efforts failed. In opposition to the *coercible* gases, he called these the *permanent* gases. But nowadays we know also these substances as liquids, the boiling points of which lie at extremely low temperatures. Faraday himself was convinced that his aim could have been attained by further refrigeration.

This conviction was rightly founded on the experiments of Cagniard de la Tour, who twenty years earlier had shown that in the case of ether, liquid and vapour became more and more nearly identical as the temperature increases, and at 194° C. they pass over into the same intermediate state, while above that temperature no liquid ether exists. Five and twenty years after Faraday, Andrews showed that in this respect carbon dioxide behaves entirely like ether, and that at 31° C. it passes over into the intermediate state observed by Cagniard de la Tour. He found that below this temperature carbon dioxide can be liquefied by the application of pressure, and that above this it is impossible; this he called the *critical temperature* of carbon dioxide, and the vapour pressure belonging to it the *critical pressure* of this substance.

Though Faraday's surmise had been rendered probable by Andrew's experiments, it was not verified until Van der Waals—henceforward our guide in this field—laid down the explanation of these phenomena in the theory of the continuity of the liquid and gaseous states of aggregation, and showed us how, from the deviations from Boyle's law for a substance investigated in the gaseous condition, the properties of the liquid into which this substance passes can be derived.

His calculations were soon to be confirmed by the experiments of Cailletet and Pictet.

In Cailletet's work the refrigeration of the strongly compressed gas by expansion is prominent, in Pictet's work the subtraction of heat.

It is to Cailletet that we owe the very useful invention of compressing relatively large quantities of gas in a glass tube under a very high pressure by means of a compression pump.

Pictet's merit consisted in showing that strong gradual cooling could be produced by circuits like those on which the ordinary sulphur dioxide ice-machine is based. In this apparatus sulphur dioxide extracts heat where it vaporises. In order to make it serve again, the vapour is led away and liquefied in another part where, while liquefying, it loses again

the absorbed heat. The liquefied sulphur dioxide may be led back to the place which is to be cooled, where it evaporates again, and thus with the same quantity of sulphur dioxide circulating in this circuit, or *cycle*, new quantities of heat may be continually extracted from an apparatus.

Pictet availed himself of such a cycle for the intense cooling of a condenser in which carbon dioxide (otherwise only liquefiable under high pressure) could then be liquefied under small pressure. With carbon dioxide we can again form a cycle exactly like the one with sulphur dioxide, and cool at the low temperatures at which carbon dioxide evaporates *in vacuo*. The two operations combined: the cycle of liquid sulphur dioxide to liquefy carbon dioxide, and the cycle of liquid carbon dioxide to keep up still lower temperatures, form a graduated fall—a *cascade* of temperatures.

As to oxygen, Pictet and Cailletet both succeeded in seeing it for a moment in the liquid state. Yet they failed to collect it as a static liquid.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, March 10th, 1905.

Dr. R. T. GLAZEBROOK, Past-President, in the Chair.

A PAPER "On Direct Reading Resistance-thermometers, with a Note on Composite Thermocouples," was read by Mr. A. CAMPBELL.

The paper describes two methods by which the reading of a resistance-box in connection with a platinum resistance-thermometer gives directly the actual temperature without the use of any formula or table. In the first method the variable resistance in the measuring-arm of the Wheatstone's bridge is shunted by a suitable resistance. When this shunt has the proper value, the change of resistance in the measuring-arm necessary to give a balance is proportional to the change of temperature of the platinum to a good degree of accuracy up to 1000° C. A more exact method (that of the "Rectifying Loop") is somewhat similar. In it the measuring-arm consists of a closed loop of resistance, one end of the arm being a fixed point on the loop, while the other end is a slide which can be moved along the loop. The total resistance of the arm is connected by a simple parabolic law with the excess X of the slider reading over a zero reading. Thus $R = A + BX + CX^2$. The author shows how the resistance of the loop and the zero reading may be calculated so as to make this parabolic formula identical with that giving the temperature-resistance variation of any specimen of platinum. When the resistances have these values, the reading X will be proportional to the temperature (Centigrade) of the platinum.

In an appendix the author points out that for measuring small temperature differences up to 100° or 150°, the most useful thermocouples are iron-nickel or iron-constantan. The voltages given by these are nearly, but not quite, proportional to the differences of temperature. In order to make the proportionality more exact, he proposes to use a "composite" (triple) junction by putting in parallel with one of the usual wires a wire of a third metal (*e.g.*, copper); by adjusting the relative resistances of the branches of this parallel circuit the temperature-voltage curve of the combination can be practically rectified.

Mr. W. DUDDELL expressed his interest in the paper, and asked the author if he had considered the question of putting a constant resistance in series with the rectifying-loop. By so doing, it would be possible to simplify the mathematical processes involved in the method. With re-

ference to the author's note on composite thermocouples, he asked if Mr. Campbell could give any information regarding the variation of the thermoelectric properties of constantan with the percentage of nickel and copper present in the alloy.

Prof. CALLENDAR said he admired the rectifying-loop method of reducing the direct readings to the gas-scale, and thought it would be useful in practical work, especially at high temperatures, but for the most accurate scientific work at moderate temperatures he thought the corrections would be too complicated, and that trouble would be saved by adopting the ordinary method. It was most important in practice to secure accurate compensation of the leads, which could be insured in a satisfactory manner only by making the leads and the ratio arms equal. Instead of making the loop-resistance equal to kR as proposed in the paper, it would be necessary to make it equal to R , and to write $x = c + mt$ or its equivalent. The method suggested by Mr. Duddell of adding to the loop a resistance in series equal to R_0 , would simplify the algebraic relations of the coefficients, giving $m = aR_0$, and $n = a^2R_0/b$, but would prevent the thermometer reading on the loop below 0° C. For many purposes this would not matter seriously. Neither the loop method, nor the three-lead arrangement subsequently proposed by the author, could be used with a bridge-wire, as both involved plug or sliding contacts of negligible resistance. The three-lead arrangement also precluded the possibility of making an insulation-test of the leads at any time. With regard to composite thermocouples, he did not think the arrangement would be useful except for very moderate ranges of temperature on account of the irrationality of the curves, which could not be satisfactorily represented by parabolic formulae. He had himself employed a similar arrangement with resistance-thermometers, combining wires of different materials in series, such as platinum and gold, or platinum and iron, so as to eliminate the b term. This was a simple and fairly reliable way of rectifying the curve, since the resistance-variation of most metals followed approximately parabolic formulae, and the sign of b was positive for many metals but negative for platinum. It was difficult, however, to find a suitable metal capable of standing high temperatures without change.

Dr. CHREE pointed out that the resistance of the coils and shunt would vary somewhat with temperature unless made of some material with a negligible temperature coefficient. This would presumably necessitate some correction to the reading in the ordinary case. He asked Mr. Campbell whether a change in the total resistance of the wire due to temperature affected in any way the accuracy of the calculations.

The CHAIRMAN expressed his interest in the paper and in the usefulness of the methods described for ordinary work, but pointed out that for the most accurate work it was advisable to work with the simplest possible form of apparatus, and to apply the necessary corrections at the end. With regard to the question of compensation raised by Prof. Callendar, the mathematics given in the paper would embody his suggestion if x_0 were given a suitable value instead of being made equal to unity. The constantan wires referred to by Mr. Campbell had been tested over a large range of temperature, and it had been found that a constantan-iron couple gave a linear formula.

Mr. CAMPBELL, in reply to Prof. Callendar, said it would be possible to arrange the rectifying loop with plug-contacts instead of sliders; with 25 ohms in the measuring arm, sliders could not cause serious error. In reply to Mr. Duddell's second question, he did not know if any of the other copper-nickel alloys gave better thermoelectric results (against iron) than constantan. In both of the rectifying methods the temperature-coefficient of the measuring arm caused no more error than in the ordinary method. In further answer to Prof. Callendar's and Mr. Duddell's remarks, he mentioned that for both methods he had indicated clearly in the paper that when once the ratio of the resistances of the zero-reading and the total loop (or the

shunt) was found from α and β , then the absolute values of these resistances may be altered in any ratio desired. The bridge can thus have equal or unequal arms at will.

A paper "On the Stresses in the Earth's Crust before and after the Sinking of a Bore-hole," was read by Dr. CHREE.

In *Nature*, October 20, 1904, there appeared letters by Mr. G. Martin and the Hon. C. A. Parsons dealing with the size of the stresses in the earth's crust, and speculating as to what would happen if a hole were bored to a depth of 12 miles. The present paper discusses the subject, treating the earth as an elastic solid, and points out the various uncertainties that exist. Solutions are presented of a number of mathematical problems having a bearing on one or other of the possibilities discussed. The principal novel case considered is that of a composite earth, consisting of a core of incompressible material and of a crust which may be compressible or incompressible. If the earth be treated as a homogeneous and perfectly elastic solid, the mathematical solution indicates near the surface horizontal pressures which are of extremely large magnitude unless the material be supposed incompressible or nearly so. To this hypothesis there is the obvious objection that on the one hand there is no evidence of enormous horizontal pressures, while on the other ordinary materials are by no means incompressible. The hypothesis of an incompressible nucleus and compressible crust, whose thickness is but a small fraction of the earth's radius, is much more free from objections. The horizontal pressure to which it leads vanishes at the surface, and to a first approximation is like the vertical pressure, a linear function of the depth. On this hypothesis a small portion of the material at a few miles depth, before the bore-hole is formed, is similarly situated to a solid cylinder exposed to different normal pressures over its flat ends and curved surface. The vertical pressure at a given depth is shown to be similar in magnitude, but probably somewhat less than the pressure that would exist at the same depth in a liquid of the same mean density as the superincumbent crust. The horizontal pressure may be as great as the vertical pressure, but is probably less unless the material behave as an incompressible solid. After the bore-hole is formed the material immediately surrounding its walls is similarly situated to a hollow cylinder whose inner cylindrical surface is free from stress, while normal pressures act over its outer cylindrical surface and flat ends. From this conclusion must be excluded the material immediately under or close to the foot of the bore-hole. The material immediately under the hole is to a certain extent somewhat similarly situated to a cork in a gingerbeer-bottle, but under ordinary conditions the weakest point would seem to be in the cylindrical wall a very short distance above the bottom. The tendency of course is for the walls to be forced in or for the material to flow. Calculations are made as to the tendency to rupture on the maximum-stress-difference theory for the several hypotheses considered.

A paper "On the Lateral Vibration of Bars of Uniform and Varying Sectional-area" was read by Mr. J. MORROW.

Lord Rayleigh has given a method by which the approximate period of vibration of a rod can be calculated without the use of transcendental equations. The question has recently been further discussed by Mr. Garrett and Dr. Chree. The object of the paper is to show that, by assuming a type of vibration consistent with the conditions obtaining at the ends of the bar, the period can be obtained approximately in a simple manner, and that by a process of continuous approximation the period and the type of the vibration may be determined in a large number of cases with great accuracy. From the hypothetical displacement equation an expression is obtained for the bending moment at any point in the length of the bar, and from this the resulting curve of deflection is calculated by the formula $\frac{d^2y}{dx^2} = M/EI$. This curve can then be used in a second approximation to the value of M , and the process repeated until the required accuracy is reached. The cases of

Clamped-free, Supported, and Free-free bars are first dealt with, and then solutions are given for a Clamped-free bar (1) when the breadth varies as the distance from the free end; (2) when the breadth varies as the square of the distance from the free end; and (3) when the depth varies as the distance from the free end.

Dr. CHREE pointed out that the author's formulæ for the

frequency contained factors of the type $\sqrt{y/y}$. y varied, however, as $\cos kt$, and so y/y was negative. The explanation was that Mr. Morrow's "inertia forces" ought really to be taken with the reversed sign, and ought to be the "reversed effective forces" ordinarily employed in dynamical problems. He remarked that the results to which the method led were very close approximations indeed, but that the successive approximations entailed laborious algebra. The value of the method would be much enhanced if it could be shown that the phenomenon exhibited by all the cases treated by Mr. Morrow of the calculated frequency being too low was universally true. If that were the case, one would know that the correct value was intermediate between that given by Mr. Morrow's first approximation and by Lord Rayleigh's method. Dr. Chree also pointed out that Kirchhoff had obtained exact solutions for a variety of forms of varying section, and that one of his cases discussed in Todhunter and Pearson's "History of Elasticity" was the same as the last of the author's cases. In this instance the frequency obtained by Mr. Morrow's third approximation came very near Kirchhoff's exact result.

Mr. MORROW, in reply, said that by his method the first value for the frequency was generally a long way out, but that the true value was gradually approached by successive approximations. By making two approximations, therefore, it was possible in any case to determine whether the initial value of the frequency was too high or too low. The method employed by Mr. Garrett gave one approximation only, and there was no continuous approach to the true frequency.

FARADAY SOCIETY.

Annual General Meeting, March 6th, 1905.

Dr. F. MOLLWO PERKIN, Treasurer, in the Chair.

THE CHAIRMAN moved the adoption of the Annual Report of the Council and the Statement of Accounts and Balance Sheet for the period June, 1903, to December, 1904. These have already been published in the February issue of the *Proceedings*. The motion was carried unanimously.

THE CHAIRMAN said that no further nominations for Officers and Council in addition to those already announced had been made or suggested to the Council. He therefore proposed that the gentlemen already nominated be elected *en bloc*. This was carried unanimously.

The new Council is constituted as follows:—

President—Lord Kelvin, O.M., G.C.V.O., F.R.S.

Past President—Sir Joseph Wilson Swan, F.R.S.

Vice-Presidents—Prof. A. Crum-Brown, F.R.S.; Sir William Huggins, K.C.B., P.R.S.; Sir Oliver Lodge, F.R.S.; Ludwig Mond, F.R.S.; Lord Rayleigh, O.M., F.R.S.; Alexander Siemens, Pres.I.E.E.; James Swinburne, M.Inst.C.E.

Treasurer—Dr. F. Mollwo Perkin.

Council—George Beilby, Bertram Blount, W. R. Cooper, Sherard Cowper-Coles, Prof. A. K. Huntington, Dr. R. A. Lehfeldt, W. Murray Morrison, M.Inst.C.E.; Dr. W. S. Squire, Dr. O. J. Steinhart, Prof. Ernest Wilson.

Votes of thanks were then passed to the retiring President, Sir Joseph Swan; to the honorary auditors, Messrs. L. Gaster and T. M. Lowry; and to the Institution of Electrical Engineers for their generous hospitality in granting the Society the free use of their Library for the monthly meetings.

The Twelfth Ordinary Meeting was subsequently held.

Mr. F. W. HARBORD read a paper on "*Recent Developments in Electric Smelting in Connection with Iron and Steel.*"

The paper embodies the principal results of the investigations made by the Commission sent to Europe last year by the Canadian Government for the purpose of reporting upon the different thermo-electric processes for the smelting of iron ores and the manufacture of steel at work in Europe, together with some additional information bringing the subject up to date. The author acted as metallurgist to that Commission. The reading of the paper was illustrated by means of an interesting series of lantern slides.

Electric smelting furnaces are divided into three main classes:—Induction furnaces, resistance furnaces, and arc furnaces. The first type is specially adapted for melting rather than smelting; the others can be adapted for either purpose.

1. Induction Furnaces.

The best known furnace of this type is the Kjellin furnace. This is, in effect, a step-down transformer, in which the contents in the hearth form the secondary circuit of the transformer. Any grade of steel, from 0.10 to 1.50 per cent carbon, can be produced in this furnace, but high-class materials must be used, as there is no elimination of impurities. The furnace at Gysinge, in Sweden, which has been in operation since 1900, is now of 175 kilowatts capacity, and its output is 5.2 to 5.5 tons per twenty-four hours. The furnace absorbs from about 0.13 to 0.16 E.H.P.-year per ton of ingots, according to the carbon content of the product.

2. Resistance Furnaces.

(a) *The Héroult Furnace.*—A 4-ton furnace at Kortfors, in Sweden, and a somewhat smaller one at La Praz, in France, are producing high-quality steel on a considerable scale. The furnace is a tilting one, and is basic lined; two large adjustable electrodes pass vertically through the roof. In this furnace ordinary steel scrap can be converted into steel of the highest quality, the impurities being removed by suitable fluxes. Steel varying from 0.079 to 1.000 per cent carbon is made with perfect ease. At La Praz an alternating current of 4000 ampères and 110 volts is used. The furnace absorbs about 0.111 E.H.P.-year per ton of ingots in the case of low-carbon steel, and about 0.17 E.H.P.-year for high-grade carbon steel.

(b) *The Keller Furnace.*—This is similar to the Héroult furnace, differing only in details. The author saw tests made with a 35-cwt. experimental furnace at Livet. Common scrap was the raw material, and the energy absorbed was about 0.120 E.H.P.-year per ton of ingots.

(c) *The Resistance Furnace for Direct Smelting from the Ore.*—Experiments made at Livet in the Keller furnace demonstrated the possibility of making pig of the most varied composition. The type of furnace is identical with that used for making iron alloys, such as ferro-chrome, ferro-tungsten, and ferro-silicon. The furnaces at Livet are vat-shaped, and connected at their lower ends by a central well; four are usually grouped together. The current used in the trial runs varied between 10,600 and 12,000 ampères, at voltages from 63 to 68, and the energy absorbed was 0.25 H.P.-years per ton of pig for a white iron containing little silicon and manganese, and 0.53 H.P.-years for a grey iron more silicious. The coke used averaged 767 lbs. per ton of pig-iron produced, and the estimated cost of electrodes was 3s. 6d. per ton of iron.

At Livet 45 to 60 per cent ferro-chromes and 25 to 80 per cent ferro-silicons are made regularly. For such high-grade alloys the electric furnace is more economical than the blast-furnace.

The Gin Process.—In this it is proposed to dispense with carbon electrodes, using instead large water-cooled block terminals, which lead the current into a long basic-lined narrow channel, forming the furnace hearth. The author does not know whether the process has been tried on a commercial scale.

3. Arc Furnaces.

The heat is obtained from direct radiation from the arc, and by reflection from the roof and sides of the furnace.

(a) *The Stassano Furnace.*—The latest type at Turin is a 5-ton furnace (per twenty-four hours), and absorbs 4900 ampères at 150 volts, the current being distributed between two arcs (and therefore four electrodes), which meet at the centre of the furnace. The furnace is lined with magnesite bricks. Steel is produced direct from the ore (pure hæmatite) in one furnace. Reduction is effected only by the carbon, which, with the ore, is moulded into briquettes, and a practically pure iron can be obtained. The energy consumption is 0.186 E.H.P.-years per ton of steel, and the consumption of electrodes 5 k.grms. per ton of steel.

(b) *The Harmet Process.*—In one form of furnace the inventor melts oxides of iron in a vertical shaft by means of producer gas, and reduces them by solid incandescent carbon; in another form carbonic oxide is his chief reducing agent. The process has not yet been experimented with on a commercial scale.

General Conclusions.

(a) Steel, equal in all respects to the best Sheffield crucible steel, can be produced even in this country, either by the Kjellin, Héroult, or Keller processes, at a cost considerably less than the cost of producing a high-class crucible steel, assuming electric energy to cost £10 per E.H.P.-year.

(b) At present, structural steel, to compete with Siemens or Bessemer steel, cannot be economically produced in the electric furnaces, and such furnaces can be used commercially for the production of only very high-class steel for special purposes.

(c) Speaking generally, the reactions in the electric smelting furnace are similar to those taking place in the blast-furnace. By altering the burden and regulating the temperature by varying the electric current, any grade of iron, grey or white, can be obtained, and the change from one grade to another is effected more rapidly than in the blast-furnace.

(d) Pig-iron can be produced on a commercial scale at a price to compete with the blast-furnace, only when electric energy is very cheap and fuel very dear. With electric energy at 10 dols. (41s. 8d.) per E.H.P.-year, and coke at 7 dols. (29s. 2d.) per ton, the cost of production is approximately the same as the cost of producing pig-iron in a modern blast-furnace. Under ordinary conditions, where blast-furnaces are an established industry, electric smelting cannot compete; but in special cases, where ample water-power is available, and blast-furnace coke is not readily obtainable, electric smelting may be commercially successful.

DISCUSSION.

M. ADOLPHE MINET communicated some further particulars of the Héroult process, giving a sketch of its development. About 3000 tons of steel have up to the present been made. The process was an advance upon others and upon the crucible furnace, because it allowed or a complete elimination of sulphur and phosphorus, and common raw materials, costing 70 francs a ton, can be used. The current consumption at present is 120 kw.-hours per ton of steel. M. Minet also gave some tables of tensile-strengths, and summed up the special advantages of this process, and he exhibited some specimens of steel and ferro-alloys made in the Héroult furnace.

Mr. B. H. THWAITE (communicated) described a scheme for the production of high-quality ingot steel in Canada, suggested by him in 1903. The anthracite had to be imported from the United States, and it was proposed to briquette the raw materials to effect the reduction in a particular design of arc furnace. The gases evolved were to heat an open-hearth furnace in which the steel was to be made, additional electric heating also being available. He considered that both the Keller and Héroult processes were available for the useful employment of the

power-producing resources of the blast-furnace, now mostly going to waste.

Mr. BERTRAM BLOUNT (communicated) insisted that now is the time for steel-makers in this country to adopt electrical methods of working for making the special steels used in the construction of such articles as guns, safes, motor-cars, cutting tools, &c., which have individual properties easily obtained when those methods are employed.

Mr. W. MURRAY MORRISON agreed that the Keller and Héroult seemed at present the only practicable furnaces as far as this country was concerned. M. Héroult had recently reduced his energy figure to 0.15 E.H.P.-years per ton of steel, starting with scrap, and to the remarkable figure of 0.0114 E.H.P.-years (equivalent to 2s. 4d. a ton), starting with molten metal; he was now constructing a 300-ton mixer and a 50-ton furnace, in which still better results were to be hoped for.

Mr. R. S. HUTTON pointed out that electric heating was only economical when very high temperatures were desired, and that it was not, therefore, desirable to use electric furnaces for melting. One of the advantages of the Héroult furnace arose from the fact that it was an arc as well as a resistance furnace. The two sources of intense heat caused convection currents in, and hence intimate mixture of, the molten charge.

Mr. R. L. GAMLEN, speaking as one interested in the production of cheap power, was of the opinion that the limiting figure of £10 per E.H.P.-year mentioned by the author could be considerably lessened by the producers of power on a large scale. In considering this question of cheap power too much stress was usually laid on fuel costs; capital costs were an even more important item. These were very large in the huge gas engines required by low thermal-value gases, such as blast-furnace gases, and steam-power was therefore more economical even if the gas cost nothing.

Dr. O. J. STEINHART drew attention to the difficulties of making low carbon ferro-chromes, especially in arc furnaces. The value of these was very high compared with those of higher carbon content.

Mr. T. V. HUGHES said that a sober presentment of the possibilities of electric smelting, such as Mr. Harbord had given, was of great value as not tending to inflate the public mind.

Prof. F. WILSON thought that the figure of £10 per E.H.P.-year could be diminished for large supplies of power.

The CHAIRMAN, in moving a vote of thanks to Mr. Harbord, remarked on the enterprise of the Canadian Government in appointing a Commission to study this very important question. He wished that some of our manufacturers would see the desirability of becoming alive to the possible future of electric smelting and making experiments on the subject.

THE NATIONAL PHYSICAL LABORATORY.

THE Laboratory, opened by the Prince of Wales three years ago, has just issued its Report for the year 1904.

Its object is to carry out researches and investigations of importance to Commerce and Industry, and to standardise and test instruments and materials.

In addition to the grant of the site and buildings at Bushy House, it has received a sum of £19,000 for building and equipment and an annual Treasury grant of £4000. This is to be increased to £5500 this year and £6000 next, and, in addition, a grant of £5000 is to be made for further equipment; the hope is also expressed that this may be continued for some years.

While these grants do not nearly reach those made in other countries for similar purposes they will enable the useful work which is being done to be extended.

Besides the £4000 received from the Treasury, the income of the Laboratory for 1904 has been made up of donations

and subscriptions, £2300; Gassiot Fund (for magnetic work), £450; fees for work done, £6000—a total of £12,750.

Among the researches of more general interest concluded during the year are the following:—

An investigation for the Engineering Standards Committee into the properties of insulating materials at the temperatures ordinarily reached in Generators and Motors, and a study of the distribution of temperature in the coils of such machines.

An examination of the allowances necessary to secure proper working between the running parts of machinery.

An investigation into the properties of different qualities of gutta percha.

Photometric and Life Tests of incandescence lamps under various conditions.

An investigation into the methods of obtaining and measuring high temperatures of 1800° C. to 2000° C.

The erection and testing of a standard lathe for cutting leading screws for large lathes to a very high order of accuracy.

An examination of the properties of Nickel Steels, prepared for the work by Mr. R. A. Hadfield.

The construction of the electrical parts of a standard balance for the measurement of an electric current.

The construction of a machine for examining the effect of rapid alternations of stress on materials used in engineering practice.

In addition to these and other researches which have been successfully carried through, a number of inquiries have been declined for want of sufficient equipment. The committee hope that this may, however, be shortly remedied.

During the year some 28,000 instruments of various kinds have been tested. Of these, more than half are clinical thermometers. The rest comprise telescopes, binoculars, watches, chronometers, barometers, sextants, thermometers, chemical vessels, electrical apparatus of all kinds, measuring instruments, incandescence lamps, gauges, tests on fuels and on steels, and numberless other tests.

The Laboratory is under the control of an Executive Committee of which Lord Rayleigh is Chairman, and which consists of representatives of the Royal Society, the Institutions of Civil Engineers and Mechanical Engineers, the Iron and Steel Institute, the Institution of Electrical Engineers, and the Society of Chemical Industry.

The Committee meets once a month, and its members take a very active interest in promoting the welfare of the Institution.

The Committee is selected from a larger body, the General Board, which meets annually to receive and consider the Report of the Committee, and to settle on the scheme of work for the year. This meeting took place on March 17th, and on this occasion the Laboratory was opened for inspection to a number of invited guests.

CORRESPONDENCE.

A QUESTION OF NOMENCLATURE.

To the Editor of the Chemical News.

SIR,—For some time past I have noticed in the CHEMICAL NEWS the frequent use of the word "of" in such cases as, for instance, in last week's issue, "platinocyanide of barium" (p. 124), "hydrate of hydrazine" and "peroxide of hydrogen" (p. 131).

Whilst recognising that these expressions are correct as regards Continental usage, I prefer the more general English style, "hydrogen peroxide," &c. May I therefore appeal to your contributors to dispense with the unnecessary "of," which must be an eyesore to the majority of chemists.—I am, &c.,

E. T. DANIELS.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxi., No. 8, February 20, 1905.

A New Method of Synthesis of the Alcoyl Derivatives of certain Saturated Cyclic Alcohols. Preparation of Homologues of Menthhol.—A. Haller and F. March.—Under the experimental conditions used by the authors, the sodium derivatives of propylic, isobutylic, and isoamyl alcohols act both as reducing agents and substitution agents with regard to β -methylcyclohexanone, and produce homologues and isomers of menthol identical with the methylalcoylhexanols obtained by reduction of the synthetic methylalcoylhexanones. This new method produces a better yield than the old way of obtaining these alcohols, and also produces them in a single operation instead of two successive ones. The authors propose to extend this method of operation not only to other cyclic ketones, but also to the aliphatic ketones.

Application of the Method of Direct Hydrogenation by Catalysis to Nitriles. Synthesis of Primary, Secondary, and Tertiary Amines.—Paul Sabatier and J. B. Senderens.—The authors' method of direct hydrogenation in presence of reduced nickel applies equally well to formic nitriles. The reaction can generally be effected at a temperature between 180° and 220° . As in the case of all hydrogenation methods by the wet way, a primary amine is first formed, containing the same amount of carbon as the nitrile, and formed according to the equation $C_nH_{2n+1}CN + 2H_2 = C_nH_{2n+1}.CH_3.NH_2$. An application of this method of hydrogenation leads to the formation of the three corresponding amines. The results are less satisfactory when the aromatic nitriles are subject to direct hydrogenation with nickel, when the production of a carbide and ammonia tends to predominate. For instance, benzoic nitrile, when hydrogenated over nickel at 200° , produces almost exclusively toluene and ammonia.

Lactylactylactic Acid and the Dilactide of Inactive Lactic Acid.—E. Jungfleisch and M. Godchot.—Lactylactylactic acid is produced at the same time as the dilactide when very dry lactic acid is distilled at about 230° under a very small pressure. The substance separates out in the form of small colourless needles which melt at 39° and boil without decomposition at 235 – 240° under a pressure of 0.020 m.m. It is very soluble in ether, chloroform, benzene, and acetic acid, and very hygroscopic, the water finally transforming it into lactic acid. The dilactide of this substance can also be prepared.

The Carbimide of Natural Leucine.—MM. Hugoueney and Morel.—The authors prepare the carbimide of leucine, $CO-N-CH-CH_2-CH \begin{smallmatrix} CH_3 \\ \diagup \\ COOH \end{smallmatrix}$, a substance from which

the substituted ureas can be formed with usually very good results.

Perborates.—J. Bruhat and H. Dubois.—The perborates are salts of the peroxy-acid, which differs from boric acid by a molecule of supplementary oxygen. This is very stable in the amorphous and crystalline salts, even when these contain one or several molecules of water of crystallisation, but a rise of temperature or an excess of water is usually sufficient to decompose the bodies. This unstable oxygen apparently only appears to possess cohesion in the alkaline reaction which gives perborates. Free perboric acid cannot be isolated; all perborates being decomposed with liberation of the molecule of supplementary oxygen. The oxygen thus liberated combines with water to produce hydrogen peroxide.

Prediction of a Chemical Reaction forming a Mono-variant System.—Camille Matignon.—It is possible to predict chemical reactions by using, on the one hand, the law of phases or the law of mass action, and, on the other hand, another law which can be called the law of constant variation of entropy with corresponding temperatures. In the present research the author investigates reactions satisfying the following conditions:—Only solid bodies and gaseous bodies take part in the reaction, and the gaseous bodies are always in the same term of the equation. The reversible reaction, with n bodies $A \dots C$ and n' bodies $A' \dots C'$ (all solid except A , which is gaseous), is the one considered.

MISCELLANEOUS.

The Concentration of Metallic Ions in Albuminous Solutions of Nitrate of Silver.—G. Galeotti. The presence of egg albumin in solutions of nitrate of silver lowers considerably the concentration of the Ag ions. As a rule this concentration is very feeble with monophasic systems (solutions without precipitate), and, on the other hand, much greater with solutions belonging to polyphasic systems. If the amounts of nitrate of silver and water are kept constant, we observe that with very slight increases in the amount of albumin, the concentration of the Ag ions diminishes very rapidly at the commencement according to a definite law up to a point of discontinuity, from which point it falls much more slowly and tends towards a limit, no matter how much albumin may be added.—*Zeit. Phys. Chem.*, vol. xlii., p. 330.

Decomposition of Hydride of Antimony; Example of Heterogeneous Catalytic Action.—A. Stock and O. Guttman.—The authors have examined the speed of decomposition of gaseous SbH_3 ; the influence of the sides of the vessel is very manifest. If the glass is perfectly clean, the reaction, which is very slow at first, soon becomes more rapid, making an S shaped curve; if the glass is unpolished the reaction is more rapid, the curve becomes more regular, while still keeping its point of inflection. Finally, in a bulb covered with antimony on the inside, the curve, still more regular, takes a hyperbolic form. The proportion V of gas decomposed in from unity time to time t does not follow the law of van't Hoff for unimolecular reactions, but is expressed if we call x_1 and x_2 the quantities of SbH_3 remaining at the times t_1 and t_2 , by the formula $V = 2 \frac{x_1 - x_2}{(x_1 + x_2)(t_2 - t_1)}$. In calculating

x we have taken cognisance of the fact that SbH_3 is not a perfect gas. See tables in the original article.—*Berichte*, vol. xxxvii., p. 901.

The Electrolytic Reduction of Carbonic Acid.—A. Coehn and S. Jahn.—M. Lieben obtained (*Mon. f. Chem.*, vol. xvi., p. 211, and vol. xviii., p. 582) formic acid by reducing nascent hydrogen (sodium, potassium, or barium amalgam) from lyes of $NaOH$ or CO_3Na_2 in the presence of an excess of CO_2 . The authors have proceeded by electrolytic means in an apparatus with a porous diaphragm with a platinum anode and a cathode of various metals, on different solutions saturated with a current of CO_2 . Acid liquors have given no product of reduction of CO_2 ; the same is the case with CO_3Na_2 in the absence of an excess of CO_2 . But a favourable result was obtained with CO_3NaH , or, again, SO_4K_2 saturated with CO_2 (at the cathode CO_3KII is formed). With a current of 0.25 ampère, density of current = 0.001 ampère per sq. centim., we collected formic acid (0.93 gm. per 250 c.c. of solution) characterised by the formation of the salt of barium and also by its reducing power. It does not form H_2O_2 , $HCOH$, or $C_2O_4II_2$. The returns in HCO_2H are besides very variable. The electrolysis of a solution of CO_2 in pure water also furnishes very small quantities of formic acid.—*Berichte*, vol. xxxvii., p. 2836.

Hydride of Antimony and Yellow Antimony.—A. Stock and O. Guttman. When we wish to prepare SbH_3 it is best to add the antimony-magnesium alloy very gradually to dilute hydrochloric acid, and not the inverse. The density at 15° of SbH_3 , compared with the air ($B = 754$ m.m.), is 4.360, a little higher than the theoretical density. As for liquefied SbH_3 , its density is 2.26 at -25° , and 2.34 at -60° . The solubility of gaseous SbH_3 at the ordinary temperature is 0.2 vol. in water, 15 vols. in alcohol, and 250 vols. in CS_2 at 0° . The aqueous solutions are more stable than the others. The gas decomposes with explosion on contact with an electric spark or by simple calcination. It is fairly stable in the cold, provided it is kept perfectly dry. As we increase the amount of antimony the decomposition becomes accelerated. Light and radium are both without action, but the least trace of moisture helps the decomposition in a remarkable manner. In the liquid state SbH_3 is very unstable at and above the ordinary temperature. Pure oxygen or cold air react, giving $\text{Sb}_2\text{H}_3\text{O}$ and a little hydrogen. With NO we obtain NO_2 , N, and NH_3 . The electric spark in a mixture of CO_2 and SbH_3 gives Sb, H_2O , and CO. The decomposition of SbH_3 is again accelerated by NH_3 , HCl, Cl, Br, I, S, SbCl_3 , &c., KMnO_4 , KHO , &c. We can dry SbH_3 by means of CaCl_2 or P_2O_5 . Antimoniated hydrogen does not unite with BoBr_3 . The authors have also studied the physiological action of SbH_3 in great detail. It is a very energetic poison, comparable with AsH_3 . For example, mice plunged into an atmosphere of 1/100th of SbH_3 died in a few hours (dyspnoea, nervous troubles, contractions). Persons who have to do with this gas often experience giddiness and headache. If we let a current of air or oxygen bubble through liquid SbH_3 at -90° , we observe the deposition of a yellow body, soluble at this temperature in CS_2 , but extremely unstable; at -50° it is rapidly converted into ordinary antimony. We have here an allotropic modification of Sb, *yellow antimony*, comparable with yellow arsenic.—*Berichte*, vol. xxxviii., p. 885.

MEETINGS FOR THE WEEK.

- MONDAY, 27th.—Society of Arts, 8. (Cantor Lecture). "Telephony," by Herbert Laws Webb, M.Inst.C.E.
- TUESDAY, 28th.—Royal Institution, 5. "Vibration Problems in Engineering," by Prof. W. E. Dalby, M.A., &c.
- Society of Arts, 4.30. "The Manufactures of Greater Britain—Australasia," by the Hon. Walter Hartwell James, K.C.
- WEDNESDAY, 29th.—Chemical Society. Anniversary Dinner, Whitehall Rooms, Hotel Metropole, at 6.30 for 7.
- Society of Arts, 8. "British Woodlands," by Rt. Hon. Sir Herbert Maxwell, M.P.
- THURSDAY, 30th.—Royal Institution, 5. "The Reasonableness of Architecture," by Thos. G. Jackson, F.S.A., &c.
- FRIDAY, 31st.—Royal Institution, 9. "The Scientific Study of Disiects," by Prof. Joseph Wright, Ph.D., &c.
- SATURDAY, April 1st.—Royal Institution, 3. "Some Controverted Questions of Optics," by The Rt. Hon. Lord Rayleigh, O.M., F.R.S., &c.

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CHEMISTRY	J. E. MACKENZIE, Ph.D., D.Sc.
PHYSICS	A. GRIFFITHS, D.Sc.
MATHEMATICS	E. H. SMART, M.A.
BOTANY	A. B. RENDLE, M.A., D.Sc.
ZOOLOGY	H. W. UNTHANK, B.A., B.Sc.
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THE CHEMICAL NEWS.

VOL. XCI., No. 2366.

EMANIUM.

By F. GIESEL.

I. Phosphorescence Spectrum.

My investigations of the origin of the three lines (*Berichte*, 1904, xxxvii., 1696, 3964) of self-luminous lanthanum chloride containing emanium have shown that these lines do not belong to emanium as was originally supposed, but to didymium.

A commercial lanthanum chloride when dehydrated and exposed to the radiation of 0.4 grm. of radium bromide became luminescent, and showed in the spectroscope two lines whose position pointed to their identity with the lines discovered in the emanium preparation.

Pure lanthanum chloride, placed at my disposal by Herr Przibylla, gave a continuous spectrum without any indication of lines.

As the measurement of the lines presents difficulties owing to their faintness, and to the danger which long continued observation in the neighbourhood of radium preparations entails, I endeavoured to obtain a more powerful and harmless phosphorescence of the lanthanum chloride by direct addition of about 2 per cent of radium chloride to the solution. Besides the two lanthanum salts mentioned above I used intimate mixtures (about 1 to 2 per cent of the coloured earth is found to be the best mixture; but with didymium, for example, even hundredths per cent are recognisable), obtained by evaporation of the solutions of lanthanum chloride showing no lines with very small quantities of neodymium, praseodymium, and samarium. Each of these mixtures when dehydrated phosphoresced very beautifully with definite colourations; thus if the lanthanum chloride was:—

1. Pure. Colour, beautiful blue.
2. Commercial. Blue with an orange tint.
3. Mixed with neodymium. Yellowish.
4. Mixed with praseodymium. Blue with a tinge of orange.
5. Mixed with samarium. Deep orange.

With the exception of the pure lanthanum salt all the preparations showed chiefly two lines, which were visible at the first glance. With the help of Schmidt and Hänsch's pocket spectroscope it could easily be shown that these lines in the case of neodymium lay in the neighbourhood of λ 590 and λ 530, and with praseodymium at λ 530 and λ 488. Thus with the dispersion and breadth of slit used, the line λ 530 occurs with both the didymium components. With stronger dispersion with two Rutherford prisms, this line λ 530 of neodymium is resolved into a pair of bands lying close together; the line λ 530 of praseodymium gives a narrower band which fills the space between the two didymium bands. All three lines agree with those of the emanium preparation, which can also be confirmed with the help of the comparison prism.

Commercial lanthanum chloride contains only praseodymium; this praseodymium is characterised by two fainter lines in the neighbourhood of λ 620 and λ 650, besides the two lines mentioned above. In the two preparations 2 and 4, on warming, the same phenomenon occurred, namely, a powerful yellowish luminescence, when a fifth line, perhaps at λ 580, became visible for a moment. Samarium only shows two not very distinct lines approximately in the neighbourhood of λ 560 and λ 600.

As was to be expected, only the solid solutions of the coloured earths luminesced thus, and not the pure salts. How far these reactions, as opposed to the ordinary method

of the examination of the luminescence spectra in the cathode rays, can be used to show the presence of the coloured earths (*cf. Berichte*, 1900, xxxiii., 1748; 1901, xxxiv., 2460), and how the variations of the spectra are caused according to the nature of the solid solvent used or of the excitation, must next be examined.

II. Concentration of the Emanium.

An excellent method consists in making use of the power of barium sulphate, when it brings down the rare earths, of giving the preference to emanium. Even by one operation a remarkably concentrated preparation is obtained. The same method is also the best for removing larger quantities of lanthanum. Hence the rare earths obtainable from radium barium liquors are correspondingly far more active than the whole amount obtained from pitchblende if they have been subjected to sulphate precipitation once or twice. The next best method has been proved to be fractional precipitation with magnesia; like lanthanum, emanium is precipitated with the most difficulty. But all other methods which effect the separation of lanthanum, as, for example, the fractional crystallisation of the ammonium double nitrate, may be used. The lanthanum separations are the most active, and the didymium the least. Cerium more readily retains emanium, but the separations richer in lanthanum are the more active, and those richer in cerium less active. The more completely cerium is separated in purer preparations the more energetic is the phosphorescence of the chloride.

III. Emanium X.

By analogy with the nomenclature introduced by Rutherford in the case of thorium, it is best to denote the active substances (*Berichte*, 1904, xxxvii., 3965) separated by ammonium from emanium as emanium X or "EX." Whether the further theoretical conclusions, which Rutherford connects with this nomenclature, also apply in this case, I must leave undecided. For the present I have only convinced myself experimentally that new formations take place in emanium preparations, as in the case of thorium, and that the activity of emanium is to be ascribed essentially to EX. In the small ammonium chloride residue separated we find first of all, as in Rutherford's ThX, almost all the activity of the emanation preparation.

The greater part of the EX can be separated from the burnt oxides by means of a little dilute nitric acid, so that not all the rare earths need be precipitated with ammonia.

Precipitation of EX is also brought about, according to my former article, by precipitation with barium sulphate,* but it is not complete. Whether the difference in the behaviour then observed of the active barium bromide obtained from this barium sulphate after conversion into carbonate as regards the β -radiation in solution, as compared with the strontium salt separated by ammonia, is to be ascribed to the method of separation relatively to two special substances cannot yet be determined. Once barium was separated by ammonia instead of strontium from an emanium preparation; it showed no difference in radioactive behaviour. The strontium carbonate also became thermo-luminescent in the same way as the barium carbonate—orange with a continuous spectrum. During the period of existence of these preparations, which extends to months, the thermo-luminescence can be produced at intervals as often as is required.

From concentrated solutions ammonia, among other reagents, precipitates out the greatest part of the EX. Also the part insoluble in water obtained after more strongly heating the ammonium chloride residue contains much EX.

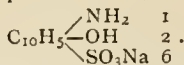
The small sulphuretted hydrogen precipitate previously obtained from EX (*Berichte*, 1904, xxxvii., 3966), or from the strontium salt, has now (after two months) quite lost the intense β -radiation, and only emits α -rays. Thus in this respect the substance behaves exactly like my "polonium."
—*Berichte*, 1905, xxxviii., 775.

* Insoluble separations from neutral or acid solution very often bring down EX (*cf. also Berichte*, 1903, xxxvi., 343).

A NEW REAGENT FOR POTASSIUM.

By Dr. EUGENIO PINERUA ALVAREZ,
Professor of Chemistry of the Faculty of Science, Madrid.

THE new reagent is a solution of 5 per cent (saturated) naphthol sodium sulphonate amide, 1.2.6 (iconogene).



This solution should be made at the time of using, employing distilled boiled cold water; if necessary, the solution can be kept in black glass flasks, filled and carefully stoppered.

The sensitiveness of this reagent is at least as great as that of platinum chloride; it may be used with ammoniacal salts, as also with magnesium salts, when the latter are mixed with the precipitates (chloride) in sufficient quantity, so as not to be precipitated by ammonium carbonate.

It is applicable to all potassium compounds in which the reaction is neutral, including the iodide.

Consequently, its use is obvious in all the cases in which we are unable to employ reagents hitherto known, as, for example, platinum chloride, sodium-cobalt nitrite, primary sodium tartrate, fluorsilicic and perchloric acids, &c.

As a microchemical agent, by the wet method, with production of crystals, it has an undoubted practical utility, because naphthol potassium sulphonate amide 1.2.6 crystallises in large, beautiful, pearly, orthorhombic plates.

In the experiments which we have made, the potassium salt analysed was the pure chloride dissolved in distilled water, containing respectively 10, 5, 2.5, 2, and 1 per cent solutions of the halogen compound.

We worked with 1 c.c. of each of these solutions, and the volume of the reagent added varied according to the degree of concentration of these solutions; the quantity by weight of chloride and of naphthol sodium sulphonate amide are always in the ratio of 1 to 3.5; by frequently shaking the test-tube when the solutions were diluted, to promote the precipitation, which is white, very brilliant, crystalline naphthol potassium sulphonate amide 1.2.6, slightly soluble in water, and completely insoluble in absolute alcohol.

The reaction is not very rapid. When the potassium solutions contain 10 or 5 per cent of chloride, the crystalline precipitate characteristic of potassium is seen in a few moments; if the amount of the potassium compound is between 5 to 3 per cent, the crystals can only be seen clearly by the naked eye after ten minutes; liquids containing 2.5 to 2 per cent of chloride take some time; and, lastly, if we mix 1 c.c. of the solution of the reagent, and shake violently, the precipitate will only be visible after several hours.

The solutions of ammonium chloride are not precipitated by means of this reagent, neither do they hinder the precipitation of potassium when the chloride of this metal is also in solution.

Salts of magnesium (Cl_2Mg), in presence of sufficient ammonium chloride to prevent its precipitation by the carbonate of the same radical, give rise to no precipitate when the reagent is added.

On working, as we have just said, with 1 c.c. of a solution containing 10 per cent of magnesium chloride, 20 per cent of ammonium chloride, and 5 per cent of potassium chloride, it was not long before the characteristic precipitate of potassium was seen, as soon as the naphthol sodium sulphonate amide was added.

A large number of soluble compounds of solutions of the heavy metals are not precipitated by this new reagent; for example, salts of iron and manganese; and, on the other hand, some are precipitated as, for example, salts of nickel and cobalt; and the precipitate of some is soluble in an excess of the precipitant, for example, the cupric salts (green solution); whilst others are not, such as bismuth.

Therefore we may state that the study of the action, which naphthol sodium sulphonate amide 1.2.6 exercises on salts in general, is of great importance for chemical analysis.

ON THE
CHEMISTRY OF INVERTEBRATE MUSCLE.

By Dr. A. B. GRIFFITHS.

IN 1892 I gave an account of the chemical composition of the nervous tissues of certain invertebrates (Griffiths, *Comptes Rendus*, cxv., 562), and in the present paper details are given of an investigation on the chemical nature of the muscular tissues of the lower animals. The following marine and fresh-water animals were selected for the purpose:—Echinodermata—*Uraster* and *Echinus*; Crustacea—*Homarus* and *Astacus*; Lamellibranchiata—*Mytilus*, *Mya*, and *Anodonta*; Cephalopoda—*Octopus* and *Sepia*.

Densities.—The densities of the muscle (water = 1000 at 15.5° C.) from the animals mentioned were as follows:—*Uraster*, 1016; *Echinus*, 1014; *Homarus*, 1021; *Astacus*, 1019; *Mytilus*, 1020; *Mya*, 1022; *Anodonta*, 1020; *Octopus*, 1026; and *Sepia*, 1030. The density of muscle is about 1055 in mammals—that is, the average density of the blood.

Lactic Acid.—The muscle of each of the animals was macerated with cold water, and the albumin in the aqueous extract was coagulated by boiling. The chlorides, sulphates, and phosphates were precipitated by the addition of lead acetate, and ammoniacal lead acetate was added after filtration. The lead was removed from the filtrate by hydrogen sulphide, and the liquid on evaporation deposited crystals of creatine. The mother-liquor, when acidified with sulphuric acid, extracted with ether, and the extract evaporated, yielded *d*-lactic acid.

The lactic acid was estimated in fresh muscle and after rigor mortis, a decinormal solution of sodium hydroxide being used for the purpose. As an example, the fresh muscle of *Homarus* gave the following result:—

26 grms. of muscle required 5.1 c.c. of N/10 NaOH for neutralisation = 0.1765 per cent of lactic acid. An alcoholic solution of phenolphthalein was used as the indicator.

With the animals mentioned in this paper the following results were obtained:—

TABLE I.
Percentages of lactic acid.

	Fresh muscle.	Muscle after rigor mortis.
{ <i>Uraster</i>	0.1641	0.4621
{ <i>Echinus</i>	0.1700	0.4658
{ <i>Homarus</i>	0.1765	0.4911
{ <i>Astacus</i>	0.2110	0.4862
{ <i>Mytilus</i>	0.1964	0.4787
{ <i>Mya</i>	0.2059	0.4799
{ <i>Anodonta</i>	0.1998	0.4698
{ <i>Octopus</i>	0.2361	0.5263
{ <i>Sepia</i>	0.2512	0.5198

There is little doubt that the lactic acid is produced from proteids, and consists of a mixture of two varieties of lactic acid—the more abundant being paralactic acid, $\text{CH}_3-\text{CH} < \begin{smallmatrix} \text{OH} \\ \text{COOH} \end{smallmatrix}$, and the other ethene-lactic acid,

$\text{CH}_2=\text{CH}_2 < \begin{smallmatrix} \text{OH} \\ \text{COOH} \end{smallmatrix}$. The paralactic acid from invertebrate muscle turned the plane of polarised light 3.4° to the right, and the specific rotation of its zinc salt = -7.54°.

Chemical Composition.—Analyses of the muscle from the nine invertebrates previously mentioned gave the results shown in Table II. (percentages).

By fractional heat coagulation, five proteids were separated from invertebrate muscle-plasma. The salted muscle-plasma was diluted to ten times its volume, and then exposed to 35° C. for two hours; a precipitate (clot) and salted muscle-serum were produced. They were separated by filtration. The precipitate consisted of myosin, which

TABLE II.

	Uraster.	Echinus.	Homarus.	Astacus.	Mytilus.	Mya.	Anodonta.	Octopus.	Sepia.
Water	83.4	82.9	85.21	86.00	80.40	80.98	81.08	76.9	77.2
So ids	16.6	17.1	14.79	14.00	19.60	19.02	18.92	23.1	22.8
1. Coagulated albumins (myosin, &c.) and their derivatives insoluble in water..	9.6	9.4	8.91	8.40	10.20	10.36	10.24	12.5	12.3
2. Soluble albumins and albuminates	3.0	3.8	2.72	2.41	3.91	4.00	3.81	4.9	4.8
3. Fat	1.4	1.0	1.23	1.20	1.40	1.43	1.45	2.8	2.6
4. Gelatin	1.3	1.1	1.02	1.06	1.42	1.40	1.42	1.3	1.6
5. Creatine	0.2	0.1	0.11	0.10	0.23	0.23	0.25	0.2	0.2
6. Ash	1.1	1.7	0.80	0.83	2.44	1.20	1.75	1.4	1.3

TABLE III.

K ₂ O	46.0	46.2	47.8	48.0	45.5	47.2	45.3	48.00	48.67
P ₂ O ₅	35.3	35.0	34.2	34.0	34.9	34.8	34.5	32.68	33.91
Na ₂ O	8.4	8.2	7.3	7.0	8.1	8.0	8.3	7.70	6.32
MgO	3.0	3.6	4.1	4.2	4.8	5.1	5.0	4.06	4.00
CaO	0.8	0.7	0.8	0.7	0.8	0.8	0.9	0.82	0.72
Fe ₂ O ₃	0.3	0.3	0.3	0.4	0.3	0.4	0.3	0.51	0.53
Cl	4.7	4.6	4.2	4.3	4.6	4.5	4.6	5.23	4.96
SO ₃	1.5	1.4	1.3	1.4	1.0	1.2	1.1	1.00	0.89

TABLE IV.

Free CO ₂ (liberated at 60° C.) ..	9.6	9.1	9.6	9.2	9.7	9.5	9.8	11.6	10.3
Fixed CO ₂ (liberated by acid) ..	1.0	0.9	1.2	1.0	1.8	1.6	1.5	2.0	1.6
Nitrogen	0.7	0.7	0.8	0.7	0.8	0.6	0.7	0.9	0.8

was re-dissolved in a 5 per cent solution of magnesium sulphate, and heated to 47° C. A precipitate was produced, which was separated by careful filtration. The precipitate was musculin or paramyosinogen, and the filtrate contained myosinogen (precipitated at 56° C.). The *salted muscle serum* was saturated with magnesium sulphate, and a precipitate produced. The precipitate consisted of myoglobulin (precipitated at 63° C.). The filtrate was heated to 73° C.; a solid and a fluid separated. The former was albumin, and the latter contained myoalbumose or myoproteose (not precipitated by heat). Musculin, myosinogen, and myoglobulin are globulins.

The five bodies of muscle plasma may also be separated from each other by using solutions of magnesium sulphate and sodium chloride of different strengths.

Myosin (muscle clot) was readily extracted from invertebrate muscle by means of a solution of ammonium chloride (10 per cent), and was precipitated from solution by saturation with magnesium sulphate. This proves that invertebrate myosin is a globulin or a mixture of globulins. It was digested by pepsin, forming peptones, and, like invertebrate and vertebrate fibrin, it decomposed hydrogen dioxide. The action of dilute hydrogen chloride converted the myosin into syntonin or acid albumin.

Ash of Invertebrate Muscle.—This contains a preponderance of potash and phosphoric acid, and magnesium salts are four times as abundant as those of calcium. (See Table III.).

Gases of Invertebrate Muscle.—The results obtained (percentages) are given in Table IV. A special form of mercurial air-pump was used for the purpose.

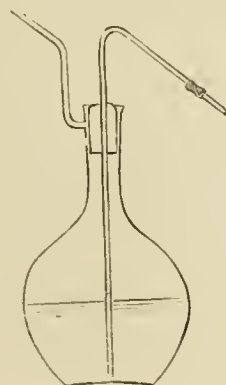
Until recently the chemistry of the Invertebrata was buried deep in primeval sameness, but with a further development of organic chemistry and analytical methods, the specialist will turn from the investigation of the functions of organs, &c., to an enquiry into the *stoffwechsel*, or metabolism, of the living body. Consequently, the more accurate determination of the properties of the compounds of the living body, in connection with the scrutiny of the minutest structure of animal protoplasm, promises to throw a clear light on the foundation of all life—the biochemical processes.

171, Brixton Road, London, S.W

A NEW WASH - BOTTLE.

By HUGO DUBOVITZ, Budapest.

THE object of the wash-bottle shown in the accompanying illustration is to enable a jet of liquid to be maintained for a considerable time without strain to the operator or danger of the vapours reaching the mouth. It is convenient for use with boiling water, H₂S water, ether, &c. As can be seen from the illustration, the whole is of glass,



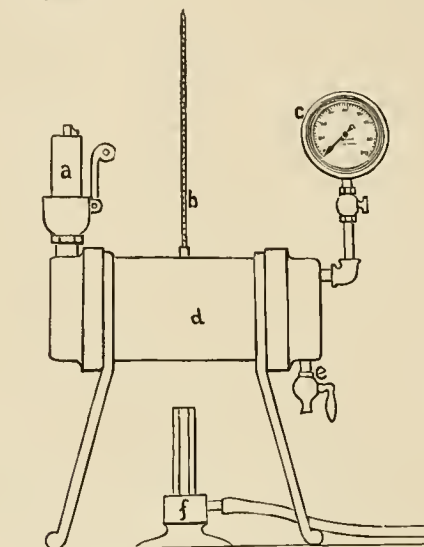
and the stopper carrying the delivery tube has a hole that can be brought opposite the blow tube, and then, when sufficient pressure has been obtained, turned on one side. The tendency for the stopper to blow out can be restrained by making it narrow and long, like the glass stopcocks generally in use. It has been found in practice that the diameter should not exceed 2 c.m. if no lubricator is used; with lubrication, a larger diameter is allowable.

The apparatus is made by the Glass-technical Institute of Erdély and Szabó, Budapest.

THE SOFTENING OF HARD WATER BY
HEATING IT UNDER PRESSURE.

By NICHOLAS KNIGHT.

IN connection with our paper in the *CHEMICAL NEWS* of August 19, 1904 (vol. xc., p. 93), on the softening of hard water by boiling under normal pressure, the question was raised as to what the effect might be of continued boiling under high pressure; that is, to reproduce the conditions that obtain in feed boilers, where the water is heated under pressure to precipitate the solids in solution. To study this question the apparatus here shown was devised and constructed by Frank L. Hann, to whom we make grateful acknowledgment.



a is a safety valve; *b* a thermometer, extending into the boiler $3\frac{1}{2}$ inches by means of a tube closed at the lower end; *c* is a steam-gauge for noting the pressure; *d*, body of the boiler, made from 5-inch heavy gas-pipe closed at each end with heavy caps; *e* is a stopcock for removing the water; *f* is a triple burner. The capacity of the boiler is about 1800 c.c. Before using the apparatus, it was subjected to a hydraulic test of two hundred pounds pressure.

There was placed in the apparatus 1200 c.c. of the hard water. Heat was applied with triple burners until the steam-gauge indicated a pressure of 90 to 100 lbs. It was not necessary to use a thermometer, as, according to Regnot's tables of the tension of aqueous vapours, the temperature would be about 156°C . This temperature was maintained with a triple burner for thirty minutes. The apparatus and contents were allowed to cool, and the water was drawn off into a glass-stoppered bottle. Then 500 c.c. were filtered and evaporated to dryness in a weighed platinum vessel of 125 c.c. capacity. The residue was heated at 110° to constant weight. The numbers express the amounts of the various constituents in 100,000 parts of the water.

Total solids in platinum vessel ..	16.52
CaSO ₄	3.43
CaCO ₃	3.90
MgCO ₃	4.61
SiO ₂	1.70
Fe ₂ O ₃	0.18
NaCl and KCl	2.70

16.52

The analysis of the raw water drawn at the same time resulted as follows:—

Total solids in platinum dish ..	30.58
CaSO ₄	3.43
CaCO ₃	12.65
MgCO ₃	10.69
SiO ₂	1.70
Fe ₂ O ₃	0.18
NaCl and KCl	2.70

31.35

For purposes of comparison, the analysis of the water pumped from the same well in April, 1904, is here given. This sample was boiled vigorously with a triple burner for twenty minutes at normal pressure.

Total solids in the platinum dish	19.18
CaSO ₄	0.98
CaCO ₃	4.25
MgCO ₃	8.52
SiO ₂	1.66
Fe ₂ O ₃	0.27
NaCl and KCl	2.34

18.02

The analysis of the raw water drawn at the same time as the foregoing resulted as follows:—

Total solids in the platinum dish	28.86
CaSO ₄	0.98
CaCO ₃	12.47
MgCO ₃	10.42
SiO ₂	2.12
Fe ₂ O ₃	0.26
NaCl and KCl	2.34

28.59

The difference between the raw water analysed in April, 1904, and again in October of the same year is mainly due to an increased amount of calcium sulphate at the latter date. The other constituents remained quite constant.

These investigations revealed the fact that the well, 330 feet in depth, from which the water was taken, receives a considerable surface drainage at certain times of the year. This causes the solids in solution to vary in amount. Comparing the effect of boiling the water under normal pressure with boiling it under a pressure of six or seven atmospheres, it is seen that the precipitation of calcium carbonate is substantially the same in each case, while the precipitation of magnesium carbonate is increased by the difference between 8.52 and 4.61 or 3.91 by the greater pressure. Boiling for twenty minutes under the normal pressure removes 44 per cent of the temporary hardness—that is, the calcium and magnesium carbonates. At the increased pressure 63.5 per cent is removed. The water, therefore, cannot be said to be softened by either process. It was found, as explained in our previous paper (*loc. cit.*), that, on treating the raw water with lime water in the ratio of 6 to 1, 71.42 per cent of the temporary hardness was removed.

The experimental work was done by C. G. Eldredge, Assistant in the Cornell College Chemical Laboratory.

Mount Vernon, Ia., March 8, 1905.

Special Constituents obtained during the Tempering of an Aluminium Bronze.—Pierre Breuil. —The author investigates the properties of an alloy of aluminium and copper which melts between 1010° and 1030° . When tempered at different temperatures the alloy presents a different microscopic structure. — *Comptes Rendus*, cxli., No. 9.

THE IMPORTANCE OF ACCURATE MEASUREMENTS AT VERY LOW TEMPERATURES.*

By Dr. H. KAMERLINGH ONNES.

(Continued from p. 139).

SUCH was the state of experimental physics when more than twenty years ago the pumps of Cailletet and Pictet were called at Leiden indispensable laboratory apparatus (H. Kamerlingh Onnes, "De beteekenis van het quantitatief onderzoek in de Natuurkunde," Inaugural oration, Leiden, 1882). That industrial apparatus used to become indispensable in experimental thermodynamics, that engines would have to drive compressors and vacuum pumps, was foreseen by only a few at that time.

Nobody could doubt any longer when Wroblewski and Olszewski soon after liquefied in glass tubes oxygen and the other permanent gases, with the exception of the ultra-permanent hydrogen.

It then appeared how very important a cooling agent ethylene (proposed by Cailletet) was for the range below -100°C . By evaporating this gas *in vacuo* Wroblewski and Olszewski succeeded in reaching -139°C ., far below the critical temperature of oxygen. Without an engine the great quantity of vaporising ethylene could not have been controlled, and this result could not have been attained.

Wroblewski and Olszewski, however, had no more the free disposal of liquid oxygen as a refrigerant than Faraday had that of carbon dioxide before Thilorier had succeeded in producing it in large quantities and in collecting it in the open air.

Great exertions and immense appliances had been required for the liquefaction of oxygen in a glass tube. But for further progress it was necessary that this substance (of which the boiling-point lies at the extremely low temperature of -182°C ., and which had been collected only by thimblefuls) could be poured off by litres. Only as recently as about ten years ago was this accomplished. The solution of this problem had been searched for for years, as afterwards appeared, simultaneously at Cracow, at London, and at Leiden.

I mention Olszewski's attempt because he was the first to collect liquid oxygen, while boiling in the open air, in a beaker. Only in small quantities, however. Though for some experiments this may be useful, liquid oxygen had thereby not yet become a cooling agent.

At Leiden we succeeded in arranging a third cycle of oxygen by means of a cascade of methyl chloride and ethylene, the gases being condensed in coiled tubes surrounded by the refrigerant (cf. *Communications from the Physical Laboratory at the University of Leiden*, No. 14, 1894; in Nos. 51, 54, 83, 87 are given further particulars). This cycle gives a continual stream of liquid oxygen, which produces the desired cold, and which enables us to keep up as long as we wish a bath fit for a great variety of experiments.

This success was due largely to a considerable saving of the cold obtained in the cascade process. In each cycle the cold vapours which are sucked away (in so far as they do not serve to protect from conduction of heat) pass over spirally wound tubes that admit the gas we want to condense, and thereby cool it even before it enters the condenser. The *regenerator spiral* is arranged so that the cold of the gas streaming off is wholly transmitted to the gas admitted. A similar arrangement had formally been used in the production of cold; at Leiden it was consistently applied in the cascade method, which it has adapted for the production of the lowest temperatures.

At Cracow and at Leiden the experimenters preferred to keep in the immediate neighbourhood of the apparatus in which the refrigerant was produced.

In the meantime an entirely new path had been struck by Dewar with respect to investigations at low temperatures. He learned to make glass vessels, beakers, bulbs, and glasses in which liquids with boiling points at very low temperatures could be kept and transported. These *vacuum vessels* have double walls which are silvered on the inside, while the space between them is exhausted to the utmost. The access of heat from without is now diminished to such a degree that the liquid does not evaporate perceptibly. By means of this invention we gained the desired free disposal of refrigerants like liquid oxygen.

By means of liquid oxygen, which, owing to the constancy of its boiling point, offers many advantages for measurements, the ordinary air of the atmosphere is very easily liquefiable, and the latter has the advantage with respect to waste in storage and during transportation that the raw material does not cost anything.

And thus, sooner than Wroblewski could have expected, his prophecy has been verified, that air would be the refrigerant of the future.

A great promoter in the spreading of this cooling agent has been the ingenious invention of Linde, that merely the forcing of strongly compressed air through a *regenerator spiral* at the end of which it expands, is sufficient to make it run out from the spiral as a liquid. Apparatus built for several laboratories on Linde's principles, which so happily complete the cascade method, have proved very useful, although, in order to obtain relatively small quantities of liquid air, compressors are required which compress very large quantities of air to a very high pressure. Without vacuum vessels we could not have availed ourselves of these apparatus.

Dewar's magnificent invention may be called the most important appliance for the operations at extremely low temperatures. The open vacuum flasks are for the permanent gases, while the steel bottles tested at 250 atmospheres are for the coercible gases. In fact the moment when a vacuum glass containing liquid oxygen was offered to the Prince of Wales at the meeting of the Royal Institution, marks a new era in low temperature research.

With liquid air vaporising in a vacuum we easily produce a temperature of 200°C . below the freezing-point. It has been calculated that the greatest imaginable cold in the scale of *absolute temperatures* lies 273 degrees below the freezing-point. The zero in this scale has been put at the greatest imaginable cold, and the freezing-point in this scale, which will be exclusively used in future, is indicated by 273° . The absolute temperature of air vaporising in a vacuum is no higher than 73° . Must we infer from this that the greater part of the road towards absolute zero has been covered? On the contrary. In the problem of refrigeration the degrees acquire greater significance the nearer we get to the absolute zero. In the same way the same angle of view of an observer standing on a straight road lined with telegraph-posts contains a greater number of them as he directs his eye more in the direction of the road.

By estimating as of equal importance those steps by which the distance to absolute zero is reduced in the same proportion, we get a truer view of the decrease of that distance, than by simply counting the number of degrees got through. However numerous the steps taken, the absolute zero is never actually reached.

According to this measure we may also form a true idea of the requirements for the liquefaction of hydrogen (cf. *Communications from the Physical Laboratory at the University of Leiden*, 1896, No. 23). Its critical temperature is more than twice as low as the lowest temperature that can be produced with liquid air. The accurate measurements of both Wroblewski and Olszewski had produced this datum wanted in the first place. The new leap forward to liquefy hydrogen by means of liquid air was greater than that to liquefy oxygen without the help of any frigorific agent. Much ingenuity, perseverance, and intrepidity were required to decant a beakerful of liquid

* Address delivered in commemoration of the 329th Anniversary of the University of Leiden. From *Communications from the Physical Laboratory at the University of Leiden*, Suppt. No. 9 to No. 85—96.

hydrogen from regenerator spirals which had to be enclosed in the limited spaces of vacuum vessels. Its cold is so intense that the air itself condenses and freezes, in the same way as the water vapour of the atmosphere forms a coating of hoar-frost on tubes cooled with liquid air, and blocks them.

In May, 1898, Dewar could telegraph to Leiden:—"Hydrogen . . . liquefied." A new glorious triumph was won by him. At length the victory was gained on the last of the remaining gases which had resisted Faraday's efforts. Fifty years of experimental work was the price of the whole struggle, though it seems as if each conquest is a direct consequence of the preceding. Gigantic mental activity has gone to realise Faraday's conception, and to bring all the substances known to him in the liquid and the solid state of aggregation.

Faraday's expectations have been far surpassed in this, for by the help of hydrogen which, according to Dewar has a critical temperature of from 29° to 33° , a boiling-point of 20° , and a melting-point of no more than 15° absolute temperature, experiments have become possible which he could not have imagined.

In the realisation of entirely new possibilities technics rivals with experimental physics. The former nearly always follows close in the wake of the latter; the impulse received, it rewards by placing invaluable appliances destined for society at the disposal of further scientific researches.

Also in the branch considered here the experiments made in the laboratory have given rise to an immense development of technics. The milligrammes of ammonia of van Marum, the grammes of carbon dioxide of Faraday have grown to hundreds of thousands and millions of kilogrammes. Cooling machines operating with liquid gases render the work in breweries and abattoirs efficient, render life bearable on board ocean steamers, and in the tropics. Carried in hundreds of thousands of steel boxes, rolled of red-hot steel by means of the Mannesmann process in as short a time as the glass-blower forms his flasks of liquid glass, carbon dioxide travels through all countries to be used in the preparation and decantation of effervescent beverages, in the extinction of fires, and in a great many more cases. Krupp cools his cannons with it in the process of shrinking. Sulphur dioxide is carried by rail in tanks from roast furnaces to manufactories. For the preparation of liquid air, machines of 100 horse-power have been constructed; distilleries of air for the production of cheap oxygen are being designed.

No wonder that the limit between what are called large and small appliances in experimentation changes rapidly. The appliances Faraday used, the quantities of carbon dioxide with which he worked, were the largest of his time, whereas at present every student in the laboratory disposes of them without stint. A younger generation will use the appliances which have been constructed in the laboratories after years of labour almost thoughtlessly, and as a matter of course.

It is a mere requirement of our time that the Leiden laboratory has always in store a quantity of liquid air for the use of its own pupils and for several scientists in Holland, to whom it has often been sent on application. And yet, behind what almost insuperable difficulties did this goal lie twenty years ago! Any one who then wanted to introduce the new method of working—in other words, any one who wanted to avail himself of industrial appliances in order to obtain low temperatures—would largely experience all the difficulties accompanying this. It may be that he himself had daily to take part in all sorts of manual labour, which now is exclusively done by workmen, in order to make the appliances meet the requirements of the laboratory. These difficulties still increased because the physicist himself had often to prepare ethylene in large quantities, an operation which would produce enormous excitement in a physical laboratory of the old style.

It is indeed a great privilege when technics, entering the field with a few to immediate usefulness, takes such work

out of the hands of the experimenter, and frees him from the obligation of spending time in the arrangement of auxiliary means; when it sets aside the limitations which he had to put on his investigations; and lastly, when, for him who had to vanquish all these obstacles, it comes to complete the work done instead of substituting it.

So rapid is the progress in a field where science and technics go hand in hand that the experimenter, who has at last reached the object which he has been pursuing for years, must again regard the situation as unsatisfactory as when he first set out to attain the goal.

Many improvements have been made at Leiden during the last two decades. Let us remember the battery of Bunsen elements, which, when there was not yet a single engine, had daily to be mounted and dismounted under personal superintendence, lest it should soon become unserviceable and the lamp not burn properly. Remember the first gas-motor of which the fly-wheel often would not move unless the director and the assistants had worked themselves out of breath, and also the gloomy small cellar with a wooden lathe for the instrument maker.

With this compare the steam and electrical installations in the present engineering workshop, the machinery and the useful arrangements for operations with, and for storage of, liquefied and compressed gases.

Look also at the spacious instrument maker's workshop arranged so as to meet the requirements of the time, where the students of physics themselves take part in the construction and the keeping in repair of the appliances for the experiments.

Notice the progress as manifested by the many-sided training for instrument makers at the laboratory, which, largely owing to the munificence of the liberal philanthropist P. W. Janssen, was started there during his life for the benefit of the best pupils of our excellent technical schools. Thanks to this training-school Leiden may still be rightly called the town of Musschenbroek.

All this is very gratifying, and yet if we look ahead another two decades, what a different growth (even if in another direction) will be required to keep up with the demands of the immediate future. We need think only of the newly discovered but not yet liquefied helium, of which, in the first place, the critical temperature must be ascertained by accurate measurements. And when we come to operate with liquid helium as we now do with hydrogen, will not a still more volatile coronium or nebulium be detected?

(To be continued.)

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, March 24th, 1905.

Prof. J. H. POYNTING, F.R.S., President, in the Chair.

MR. W. C. CLINTON read a "*Note on the Voltage Ratios of an Inverted Rotary Converter.*"

The values of the voltage ratios usually given for an inverted rotary converter make no allowance for the resistance of the armature. In this note terms due to the effect of armature resistance are introduced into the ordinary theoretical equations. The resultant voltage on the alternate current side is found to be less than that given by the usual rule. The calculation is only made for open circuit conditions on the alternate current side.

A paper "*On the Flux of Light from the Electric Arc with varying Power Supply,*" was read by Mr. G. B. DYKE.

The paper records the results of experiments made on the electric arc with the following objects:—1. To obtain a series of curves for alternating and continuous arcs of different lengths showing the relation between the mean

spherical candle-power and the power supplied to the arc. 2. To compare the efficiencies of the alternating and continuous arcs under different conditions of arc length and power-supply.

The subject being too wide to deal with in its entirety, the following restrictions were made:—The carbons used were 12 m.m. diameter cored (upper) and 10 m.m. solid (lower). The frequency of the alternating current was 80 cycles. The mean spherical candle-power was determined directly by means of an integrating photometer described by the author in a paper read before the Society in November, 1904. Curves connecting the M.S.C.P. with the watt are given for eight arc-lengths varying from $\frac{1}{8}$ " to $\frac{7}{8}$ " for both continuous and alternating currents. These curves are found to be straight lines which cut the axis of watts at points between 200 and 400 watts. Alternate and continuous current curves for the same arc-length are found to meet the axis of watts in the same point, showing the equality of the losses by dissipation of energy in other forms than that of light. For normal arc-lengths the alternating current efficiency is about $\frac{2}{3}$ of the continuous current efficiency. If the arc length is reduced below $\frac{1}{8}$ ", the alternating current curve rises towards the continuous current curve until, at an arc-length of about $\frac{1}{2}$ ", the two efficiencies practically coincide. On further reducing the arc-length, the alternate current curve rises above the continuous current curve. An approximate analysis of the case of equal efficiencies is given, the results of which give an arc-length similar to that obtained experimentally.

Dr. J. A. FLEMING congratulated the author, and referred to the practical value of the experiments. The ordinary method of comparing lamps by their M.H.C.P. was unscientific. What was wanted was the total flux of light per watt, and this important figure was obtained at once by the integrating photometer used by the author. Prof. Fleming instanced the case of a Nernst lamp and an ordinary carbon-filament lamp, pointing out that the ordinary tests indicated that the Nernst lamp was twice as efficient as the ordinary lamp, whereas a comparison of the total flux per watt showed an increased efficiency in the Nernst lamp of only 25 per cent.

Mr. PATTERSON expressed his interest in the paper, and referred to the photometrical work at present being carried out at the National Physical Laboratory. He pointed out that the variation of the light from an electric arc necessitated a great number of readings in order to get a satisfactory mean value. The photometer used by the author only integrated the light in one plane, and it would be more satisfactory to integrate in two planes at right-angles to one another.

A paper "On the Application of the Cymometer to the Measurement of Co-efficiencies of Coupling of Oscillation Transformers" was read by Dr. J. A. FLEMING.

This paper deals first with the latest pattern of instrument, called by the author a Cymometer, designed for the measurement of the frequency of electric oscillations, and also the length of long electric waves.

It consists of a sliding tubular condenser, consisting of two brass tubes, separated by a thin ebonite tube, the outer tube being capable of sliding off the inner tube. Parallel with this sliding condenser is placed an inductance-coil or helix, of bare copper-wire, wound on an ebonite tube. The outer brass tube of the sliding condenser carries a collar, which in turn carries a rod with a crutch at the end resting upon the inductance coil. The circuit of the instrument is completed by a copper bar which joins one end of the inductance-coil with the inner surface of the sliding condenser. When the outer tube of the condenser is moved by an insulating handle, the same motion reduces equally the capacity of the condenser and the portion of the inductance-coil included in the closed circuit. The circuit therefore consists of a variable capacity and inductance in series. The author calls the square root of the product of the capacity and inductance in any position the *oscillation constant* of the instrument. A scale is provided parallel

with the inductance-coil, on which is engraved the oscillation constant and the corresponding frequencies connected therewith by the formula $n = 1/2\pi \sqrt{CL}$.

In addition to this, the instrument is provided with a vacuum-tube, preferably a neon vacuum, which is connected between the inner and outer surfaces of the condenser. The instrument is used in the following manner:—

The copper bar is placed parallel and near to a circuit in which oscillations are taking place, and the handle of the instrument is moved, thus varying the oscillation constant, until the vacuum tube glows most brightly. Under these circumstances, it is known that the circuit of the cymometer is in resonance with that of the circuit being tested, and their oscillation constants are therefore the same, hence the scale reading gives the product of the capacity and inductance of the circuit being tested. The instrument is also provided with a rectangular wire circuit, the inductance of which is known. If this circuit is joined up with any unknown capacity and oscillations set up in it, the cymometer can be used as above to determine the product of capacity and inductance in the circuit being tested, and the inductance being known the capacity is therefore known also. Again, if we have any oscillation transformer, we can join up the primary and secondary circuits, so as to inductively oppose or aid one another. If we call L and M the inductance of the primary and secondary circuit respectively, and M their mutual inductance, the effective inductances, L_1 and L_2 , of the two circuits joined in the two ways are respectively given by $L_1 = L + 2M + N$, $L_2 = L - 2M + N$. Hence we have—

$$M = \frac{L_1 - L_2}{4} \text{ and } L + N = \frac{L_1 + L_2}{2}.$$

If, then, either L or N is separately measured, and if the resultant inductance of the compound circuit is measured, we can find the coefficient of coupling, $\frac{M}{\sqrt{LN}}$, of the

oscillation transformer. The inductance of any circuit can be ascertained for the high frequency currents by the cymometer in the following manner:—The circuit to be tested is joined up in series with a known capacity, and the rectangular circuit provided with the instrument. Two measurements are then made—(1) When the inductance to be tested is included in the circuit, and (2) when excluded from it. If the observed oscillation constants under the two conditions are called O_1, O_2 , then we have the following expression for the unknown inductance:— $L' = \frac{O_1^2 - O_2^2}{C}$.

The instrument can also be used for measuring the oscillation constant or the frequency in an open oscillating circuit, such as that of a wireless telegraph aerial, and by means of it the wave-length which is being sent out from the aerial can be measured, and also the wave-length of waves being received on any aerial. The instrument can also be employed to analyse a compound oscillation taking place in a circuit and determine the component frequencies. If thus acts as an electrical equivalent of a spectroscope.

Dr. W. WATSON expressed his interest in the paper, and said that the cymometer, on account of its simplicity, would be useful for lecture purposes. He asked Dr. Fleming if he thought that any of the anomalous results which had been obtained in determining specific inductive capacity by methods involving the mutual induction between two circuits might be due to the fact that oscillations of two different frequencies were induced in the secondary circuit. How did a change in the coefficient of coupling affect the energy transmitted to a secondary circuit?

Prof. A. W. REINOLD said that the accuracy of the experiments depended upon the use of neon tubes, and he expressed the hope that it would soon be possible to obtain them easily. Referring to the fact that oscillations in a circuit containing capacity and inductance induced in a neighbouring circuit oscillations of two distinct periods, he asked Dr. Fleming what it was that determined the energies of the two oscillations. He also asked how, when

measuring the wave-lengths of waves incident on an aerial, the fact that two oscillations were necessarily induced in the cymometer affected the utility of the instrument.

Mr. A. CAMPBELL pointed out that ebonite was used as the dielectric in the sliding condenser, and asked if there was any variation in the capacity with change of frequency.

Dr. FLEMING, in reply to Dr. Watson's question, said that undoubtedly errors might result in employing methods involving the mutual induction of two circuits for the determination of specific inductive capacities, if the observer were not acquainted with the peculiarities of coupled circuits and high frequency oscillations. The general theorem involved is that if there be two circuits each having inductance and capacity and oscillations are set up in one circuit by disruptive discharge in the other, then we have a compound oscillation set up in the secondary circuit which may be resolved into two frequencies which are different from the free natural frequency of each circuit separately. The theory has been fully worked out by A. Oberbeck (*Wied. Ann. der Physik*, 1895). Hence if it were assumed that the resulting oscillation in the secondary circuit, even if it had the same natural period as the primary, was a single oscillation of the same period, an error would undoubtedly be made. Oberbeck has not given expressions for the respective energies of the two oscillations, but he has shown that the two oscillations have different damping. The coefficient of coupling determines the respective energies of the two oscillations, but Dr. Fleming said he had not yet given sufficient attention to the theoretical side of the subject to be able to furnish expressions for the energies of the two oscillations. In reply to Prof. Reinold, he said that if the mutual inductance between the aerial wire and the cymometer were small, as it was in the case of the instrument exhibited, then the cymometer only detected the oscillations which existed in the aerial. There was no creation of duplicate oscillations in and by the cymometer itself. In reply to Mr. Campbell, Dr. Fleming said that it had been shown by Prof. J. J. Thomson and others that the variation in dielectric constant with frequency was very small or even absent in the case of ebonite. That was the reason why ebonite was chosen for the dielectric tube. In the case of glass there is a large change in dielectric constant with frequency. As regards the commercial production of neon vacuum-tubes, that subject was engaging his attention, and he hoped that they might soon be placed on the market. The beautiful process devised by Sir James Dewar of absorbing the common constituents of air by coconut charcoal at low temperatures enabled neon and helium to be prepared from the air without much trouble.

NOTICES OF BOOKS.

Chemical Statics and Dynamics, Including the Theories of Chemical Change, Catalysis, and Explosions. By J. W. MELLOR, D.Sc. (N.Z.), B.Sc. (Vict.). London, New York, and Bombay: Longmans, Green, and Co. 1904.

IT is to be expected that a text-book from the pen of this author will furnish numerous examples of lively and graphic writing, and this expectation is by no means disappointed. An excellent comprehension of the difficulties likely to occur to the student during his reading, and a peculiarly apt way of stating facts and theories in such a manner as to fix them most firmly in the memory, combine to produce a book in which the elements of a subject mostly regarded as uninteresting, and even distasteful, are treated so attractively that the student's attitude towards it should be completely changed. The work is tinged as little as can reasonably be expected by personal prejudices, and the student is cleverly carried on from the easier to the more difficult problems. The treatment of electrolytic dissociation appears to be particularly satisfactory, and it would be difficult to find another book in which an equally

useful summary of the subject is given. It seems a pity that room could not have been made for some discussion of the outlines of Kahlenberg's views on the ionic hypothesis, the student being referred to the regular text-books for evidence in favour of the hypothesis, and to Kahlenberg's articles in the *Journal of Physical Chemistry* for his views. A subject of such importance might with advantage have been given some brief attention, especially as it presents many difficulties for the unaided student. Some parts of the introduction dealing with elementary conceptions regarding velocity might have been curtailed, and some exception may be taken to the statement also in the introduction regarding the exchange of heat between two bodies at the same temperature. In fact, upon the whole, the introduction represents the least satisfactory part of an excellent book.

The Principles of Chemistry. By D. MENDELEEFF. Third English Edition. Translated from the Russian (Seventh Edition) by GEORGE KAMENSKY, A.R.S.M., and Edited by THOMAS H. POPE, B.Sc., F.I.C. London, New York, and Bombay: Longmans, Green, and Co. 1905.

THE translation of this text-book, in which the original has been followed as literally as possible, will be found of almost incalculable value to English students of chemistry. The preface to the last Russian edition, which here appears for the first time in English, is exceedingly interesting, and excellently illustrates the philosophic spirit of the great chemist, who in it has written more authoritatively than hitherto. The text-book in all probability needs no recommendation to chemists of any nation, who are already aware of its unique value. This edition includes an article on the Elements of the Rare Earths, by Prof. Brauner, of Prague, which gives an excellent summary of the characteristic properties and reactions of these elements and their separation. Another new feature in this edition is the article recently written by Prof. Mendeleeff entitled "An Attempt towards a Chemical Conception of the Ether."

Jahrbuch der Elektrochemie und Angewandten Physikalischen Chemie. ("Annual of Electrochemistry and Applied Physical Chemistry"). Reports for the Year 1903. Edited by Dr. HEINRICH DANNEEL. Tenth year. Halle-a-S.: Wilhelm Knapp. 1905.

THE delay in the appearance of this "Jahrbuch der Elektrochemie" for 1903 until the beginning of 1905, while perhaps almost unavoidable, is greatly to be regretted, and it seems probable that a better purpose would be served if it were made somewhat less complete if by that means it could be produced earlier. This volume, which is the first upon the title-page of which not one of the names of the original founders of the "Jahrbuch" appear, exceeds its predecessors to a considerable extent in size, and some important chapters on the Periodic System, the Phase Rule, the Applications of the Law of Mass Action, and Hydrolytic Phenomena have been inserted. Technical and Applied Electrochemistry are, as previously, given special attention, and with the exception of the fact above alluded to, that the late appearance may be a cause of inconvenience to those who rely upon the "Jahrbuch" for keeping themselves up to date in the study of electrochemistry, this volume, which is quite on a level with former volumes, will no doubt be found equally useful.

Techno-Chemical Analysis. By Dr. G. LUNGE. Authorised Translation by ALFRED J. COHN. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1905.

THIS small book covers a wide range of subjects, but it is difficult to see for what class of readers it is intended. The analytical chemist will find it far too short and sketchy to be of any assistance to him, and the same applies to the

technical student, for whom, moreover, the experiments chosen and products examined are hardly sufficiently typical to provide the most satisfactory course. After a few pages on technical gas analysis, in which the manipulation of gas burettes and the determination of gases by absorption and combustion are very briefly described, the special part deals with the examination of fuels and water, the latter in reference only to its use in steam-boilers. Subsequently the technical testing of the raw materials used in various inorganic chemical industries, and of the end products, are discussed, but the size of the book is such that at the most only a few pages can be given to each of such large branches as the chlorine industry, the manufacture of artificial manures, and gas and ammonia manufacture, &c. Consequently, merely a series of short notes is given upon some methods of determination, and the extreme brevity of the directions detracts seriously from their usefulness. In some cases, moreover, the best method of procedure is not advocated; for instance, the detection of sulphuric acid in vinegar by means of the starch test may now be regarded as quite superseded by more satisfactory methods.

OBITUARY.

DR. L. BLEEKRODE.

It is with regret that we announce the death of Dr. L. Bleekrode, of the Hague, news of which has reached us at the moment of going to press. Dr. Bleekrode was an Officer of the Order of Orange (Nassau), an Officer of the Académie, an Honorary Member of the Royal Institution of Great Britain, &c. His work has been principally connected with electrical matters; his first paper, in 1867, being on "The Influence of Heat on Electromotive Force." In 1870, he wrote a paper on a "Curious Property of Gun-cotton"; other papers dealt with "Electrical Conductivity and Electrolysis in Chemical Compounds," "Observations on the Microphone," &c.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxi., No. 9, February 27, 1905.

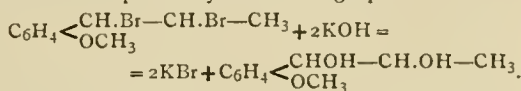
Purification of Gadolinia and Atomic Weight of Gadolinium.—G. Urbain.—The author obtains gadolinia in a state of comparative purity by fractionating the crude material separated from europium and Zr by dissolving in nitric acid of density 1.3, and then preparing the double nitrate of gadolinium and nickel, $2(\text{NO}_3)_3\text{Gd} + 3(\text{NO}_3)_2\text{Ni} + 24\text{H}_2\text{O}$. This is fractionated by crystallisation. The terbium is left in the very soluble fractions. The determinations of the atomic weight are effected by transforming the nitrate into the octo-hydrated sulphate, $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, and then obtaining the oxide Gd_2O_3 from this. The mean value obtained from fifteen experiments is 157.25 as the atomic weight of gadolinium.

Osmonitrites and an Osmium Nitrite.—L. Wintrebert.—The author prepares potassium osmonitrite, and shows how this salt can be used to prepare, either directly or indirectly, a whole series of osmonitrites, and even the corresponding osmium nitrite. The sodium, ammonium, silver, barium, strontium, calcium, magnesium, and zinc

salts are thus prepared; also osmonitrous acid, $\text{Os}(\text{NO}_2)_2\text{H}_2$, and osmium nitrite, $\text{Os}(\text{NO}_2)_3$. The remarkable stability of these bodies contrasts singularly with the properties of the osmium salts hitherto obtained. No group of salts has hitherto been assigned a representative formula. It is therefore apparent that the derived nitrites of osmium form one of the most important series of compounds of this metal.

β -Decahydronaphthol and Naphthalene Octohydride.—Henri Leroux.—When β -naphthol is hydrogenated at a temperature below 200° , under the same conditions as the author employed for naphthalene, a liquid mixture of hydronaphthols is produced, which, when subjected once more to hydrogenation, produces β -decahydronaphthol. This substance crystallises out from the less saturated compounds which accompany it. When heated in presence of potassium bisulphate it gives, when dehydrated, naphthalene octohydride.

Anethoglycol (Anethol Glycol).—E. Varenne and L. Godefroy.—When bibromanethol is treated with alcoholic potash, anethol glycol is obtained, the formation of which is explained by the following equation:—



The authors examine its properties and find that it apparently possesses peculiar therapeutic characteristics.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxxi., No. 9.

Method for the Preparation of the Aldehydes and the Methodical Degradation of Acids.—E. E. Blaise.—Already noticed.

The Condensation of the Acetylenic Ethers with Alcohols. Synthesis of the β -Acetalic Ethers.—Charles Moureu.—Already noticed.

The Decomposition of the β -Acetalic Ethers by Heat. General Method for the Synthesis of the β -Oxyalcoylised Ethylenic Ethers.—Charles Moureu.—The author has prepared six β -oxyalcoylised ethylenic ethers, four belonging to the fatty series and two to the aromatic series. These ethers are only hydrolysed very slowly under the action of ferric chloride in alcoholic solution. Their hydrolysis by warm dilute sulphuric acid has enabled the author to determine their constitution. The four ethers of the fatty series are transformed, more or less completely according to conditions, into β -ketonic ethers; the two ethers of the aromatic series when hydrolysed give almost exclusively acetophenone. The β -oxyalcoylised ethylenic ethers have higher boiling points than the corresponding β -acetalic ethers. These ethers also show an interesting anomaly in their molecular refraction (of the D line). These refractions, calculated according to the atomic refractions by the classic method, are always below the values given by the formula of Lorenz and Lorenz, $n_2 - 1M$.

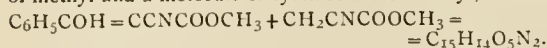
$n_2 - 2d$.
 β -Oxyalcoylised Ethylenic Acids.—Charles Moureu.—Already noticed.

Decomposition by Heat of the β -Oxyalcoylised Ethylenic Acids. Oxyalcoylised Ethylenic Carbides.—Charles Moureu.—Already noticed.

The Condensation of the Acetylenic Carbides with Alcohols.—Charles Moureu.—In the previous paper the author showed that the dry distillation of the β -oxyalcoylised ethylenic acids constituted a very regular method for the production of the oxyalcoylised ethylenic carbides having the general constitution $\text{RC}(\text{OR}') = \text{CH}_2$. With a view to preparing the bodies of the form $\text{RCH}=\text{CH}(\text{OR}')$ he has

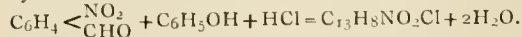
reacted directly on the acetylenic carbides, $R-C\equiv CH$, with the soda-alcohols, which easily effects the condensation of the alcohols with the acetylenic ethers, by opening the triple bond. His experiments were carried out on α -naphthylidene and phenylacetylene, and he has prepared four compounds which are fully described.

Products of Condensation of the Cyanacetic Ethers with the Acylcyanacetic Ethers.—Ch. Schmitt.—While preparing benzoylcyanacetate of methyl according to M. Haller's method, when we take an excess of cyanacetate of methyl and especially if we keep the product of the reaction on the water-bath for some time after the elimination of the last traces of methylic alcohol, we have observed, on taking up with water, the formation of a product insoluble in water and ether, fusing at 162° after several re-crystallisations in alcohol. Analysis gives it the formula $C_{15}H_{14}O_5N_2$. No doubt it corresponds to the union by aldolisation of a molecule of benzoyl cyanacetate of methyl and a molecule of cyanacetate of methyl,—



It is one of the terms of a series examined by Guichant, and like them it is not coloured by perchloride of iron, and its solutions become bright yellow in colour when treated with alkalis.

The Product of the Combination of Orthonitrobenzoic Aldehyde with Phenol in the presence of Hydrochloric Acid.—A. Guyot and A. Haller.—With the object of preparing ortho-nitrated benzaurine, the authors endeavoured to condense, in the presence of hydrochloric acid, *o*-nitrobenzoic aldehyde with ordinary phenol, but the reaction, instead of going as was expected, gave rise to an altogether different derivative. Five grms. of the *o*-nitrobenzoic aldehyde were dissolved in 4 grms. of phenol and 25 c.c. of glacial acetic acid at $50^\circ C.$, and 5 c.c. of concentrated hydrochloric acid were added. The mixture was heated on the water-bath. Yellow crystals soon appeared, and their quantity rapidly increased. After heating for three hours a crystalline magma was obtained; this was drained and washed with a little cold alcohol. The return was about 5 grms. Analysis gives the formula $C_{13}H_8NO_2Cl$; that is to say, it results from the union of equal molecules of ortho-nitrated aldehyde, phenol, and hydrochloric acid, with a loss of 2 molecules of water.



Experimental Researches on Distillation.—Eug. Charabot and J. Rocherolles.—Already noticed.

MISCELLANEOUS.

Royal Institution.—On Saturday next, April 1, at 3 o'clock, the Rt. Hon. Lord Rayleigh delivers the first of a course of three lectures at the Royal Institution on "Some Controverted Questions of Optics." On Tuesday, April 4, at 5 o'clock, Mr. Perceval Landon will give the first of two lectures on "Tibet"; and on Thursday, April 6, at the same hour, Professor Meldola commences his course of two lectures on "Synthetic Chemistry" (Experimental). The Friday Evening Discourse on April 7 will be delivered by Mr. Alfred Moseley on "American Industry"; and on April 14 by the Rt. Hon. Lord Rayleigh on "The Law of Pressure of Gases Below Atmosphere."

The So-called Peroxide of Magnesium.—O. Ruff and E. Geisel.—The peroxide of magnesium MgO_2 is decomposed at 0° at the ordinary pressure, so that we cannot collect from water any product having this composition (at most 0.67 atom of active oxygen for 1 mol. of MgO). On desiccation there is still a loss of oxygen, and there remains practically Mg_2O_3 hydrated, or $MgO \cdot MgO_2$. Gradually more oxygen is given off, and after twenty-two days at 25° or 27° there remains a product which does not lose any more oxygen, and having the composition

$3MgO \cdot MgO_2$. In the presence of water the decomposition is accelerated. The oxidation of MgO by H_2O_2 , which tends to form MgO_2 or its hydrate $Mg(OH)_4$, appears to be reversible.—*Berichte*, vol. xxxvii., p. 3683.

The Colour and the Absorption Spectra of Organic Compounds.—L. A. Tchougaff.—Observations made by the author on the absorption spectra of certain organic compounds have led him to the following conclusions:—1. The quinones and the α -diketones absorb principally the refrangible portion of the spectrum. 2. The ortho- and para-quinones show two types of absorption spectra, which are distinguished very easily one from the other. 3. In the spectra of the orthoquinones there are very well defined absorption bands; the same is not the case in the spectra of the paraquinones. 4. The orthoquinones show a very well marked limit of absorption on the red side of the spectrum; the corresponding limit with the paraquinones is, on the other hand, very vague. 5. The nitroso-compounds are characterised by an absorption band in the extreme red, which is often transformed into the absorption of the whole of one side of the spectrum.—*Journ. Soc. Phys. Chim. R.*, xxxvi., p. 189.

MEETINGS FOR THE WEEK.

- MONDAY, 3rd.**—Society of Arts, 8. (Cantor Lecture). "Telephony," by Herbert Laws Webb, M.Inst.C.E.
— Royal Institution, 5. General Monthly Meeting.
— Society of Chemical Industry, 8. "Formation of Sulphuric Esters in the Nitration of Cellulose, and their Influence on Stability," by C. N. Hake and R. J. Lewis. "The Proof of Perfusion Caps," by H. W. Brownson.
- TUESDAY, 4th.**—Royal Institution, 5. "Tibet," by Perceval Landon.
— Faraday Society, 8. "Alloys of Copper and Antimony and Copper and Bismuth," by A. H. Higns. "Refractory Materials for Furnace Lining," by E. Kilburn Scott. "Electrically Heated Carbon Tube Furnaces," by R. S. Hutton and W. H. Patterson.
- WEDNESDAY, 5th.**—Society of Arts, 8. "The Ancient Architecture of the Great Zimbabwe," by Richard A. Hall.
— Society of Public Analysts, 8. "The Determination of Higher Alcohols in Spirits," by Philip Schridowitz, Ph.D., and Frederick Kaye, A.R.C.Sc. "The Action of Slightly Alkaline Waters on Iron," by Cecil H. Cribb, B.Sc., F.I.C., and Francis W. F. Arnaud, F.I.C. "Notes on Preservatives," by Edwy Godwin Clayton, F.I.C.
- THURSDAY, 6th.**—Royal Institution, 5. "Synthetic Chemistry" (Experimental), by Prof. R. Meldola, F.R.S.
— Society of Arts, 4.30. "The Prospects of the Shan States," by Sir George Scott, K.C.I.E.
— Chemical Society, 8. "Basic Properties of Oxygen at Low Temperatures—Additive Compounds of the Halogens with Organic Substances containing Oxygen," by D. McIntosh. "Note on the Interaction of Metallic Cyanides and Organic Halides," by N. V. Sidgwick. "Chemical Dynamics of the Reactions between Sodium Thiosulphate and Organic Halogen Compounds—Part II Halogen Substituted Acetates," by A. Slater. "Chemical Kinetics of Reactions with Inverse Reactions—The Decomposition of Dimethylcarbamide," by C. E. Fawcitt. "Tautomerism of Acetyl Thiocyanate," by A. E. Dixon and J. Hawthorne. "A Method of Determining the Specific Gravity of Soluble Salts by Displacement in their own Molten Liquor, and its Application in the case of the Alkaline Halides," by J. Y. Buchanan. "The Combination of Mercaptans with Unsaturated Ketonic Compounds," by S. Ruhemann. "A New Formation of Acetylcamphor," by M. O. Forster and Miss H. M. Judd. "Preparation and Properties of 1:4:5-Trimethylglyoxal" and "Bromomethylheptylketone," by H. A. D. Jowett. "Existence of a Carbide of Magnesium," by J. T. Nance. "Action of Carbon Monoxide on Ammonia," by H. Jackson and D. N. Laurie. "Isomeric Salts of the Type $NH_4R_3H_2$ (A Correction)—Isomeric Forms of *d*-Bromo- and *d*-Chlorocamphorsulphonic Acids" and "Isomerism of α -Bromo- and α -Chlorocamphor," by F. S. Kipping. "1-Phenylethylamine," by F. S. Kipping and A. E. Hunter.
- FRIDAY, 7th.**—Royal Institution, 9. "American Industry," by Alfred Moseley, C.M.G.
- SATURDAY, 8th.**—Royal Institution, 3. "Some Controverted Questions of Optics," by The Rt. Hon. Lord Rayleigh, O.M., F.R.S., &c.

THE CHEMICAL NEWS.

VOL. XCI., No. 2367.

OBSERVATIONS ON DIPHENYLAMINE AS REAGENT FOR NITRITES, NITRATES, CHLORATES, AND ITS USE WHEN MIXED WITH RESORCIN AND β -NAPHTHOL.

By Dr. EUGENIO PINERUA ALVAREZ,
Professor of Chemistry of the Faculty of Science, Madrid.

THE majority of works on chemistry, almost all those recently published, include among their list of reagents of nitrites, nitrates, and chlorates the sulphuric acid solution of diphenylamine, and state that it produces a blue colour.

The conditions required to produce this blue colouration greatly limit the use of this reagent; indeed, if it is a positive fact that, with regard to nitrites, this colouration is almost always produced in working with quantities of very variable weights of these bodies, and with solutions of the reagent of equally varying concentration, it is not the case with chlorates and nitrates.

The colours which, in practice, are really most frequently observed are—*red-brown*, then *green*, and lastly *grey* with chlorates; and *reddish yellow*, then *green*, and lastly *dirty violet* with nitrates.

These colourations appear and disappear with more or less rapidity, and their shade varies according to the quantity of substance examined. From this it follows that, in practice, this reagent is of little use, if we only consider the colourations immediately produced.

More positive results are seen in observing the final colouration of liquids after the addition of alcohol; but, in all cases, we believe it preferable to use the fresh sulphuric acid solutions of mixtures of diphenylamine with resorcin or β -naphthol* in order to examine these substances, because the colourations are more persistent and are more easily distinguishable from each other.

We prepared a reagent with 0.1 grm. of pure crystallised diphenylamine, 0.1 grm. of re-sublimated resorcin, and on pouring 5 or 6 drops of this solution on to 0.001 grm. of the salts (nitrites, nitrates, and chlorates of the alkalis) placed in a little flat-bottomed china capsule the following phenomena are observed:—

With the *nitrites* a very permanent *yellowish green* resulted, and, after spreading out the liquid over the surface of the capsule, the edges of the spot became *blue* (especially if blown upon). By the addition of alcohol an *orange* liquid was obtained.

With the *nitrites* a *deep blue-violet* resulted, and by moving the liquid, so as to wet the whole interior of the capsule, the edges of the spot became *red*. On adding alcohol a *red* liquid was obtained.

With chlorates, the result obtained by using the reagent specified is not satisfactory; but, by replacing the resorcin with an equal weight of β -naphthol (0.1 grm.) mixed with the same quantities of diphenylamine (0.01 grm.) and sulphuric acid (10 c.c.), which composed the former reagent, we obtained, by the same process as before, a *dull green* colouration, which, after a certain time, changed to a *deep grey*, almost *black*. The liquid resulting from the addition of alcohol was *greyish or blackish*.

In order to obtain the most satisfactory results, we must call attention to the fact that, these reagents being very

highly sensitive, we cannot use a larger quantity of salt than 0.001 grm., especially in examining chlorates and nitrites.

From an analytical point of view, the practical utility of these reagents has been experimentally confirmed by the students of the Faculty of Sciences (Special Analytical Chemistry).

Laboratory of General Chemistry,
University of Madrid.

ALLOYS OF COPPER AND ANTIMONY, AND THE PHENOMENON OF TEMPER OBSERVED IN THESE ALLOYS.

By A. BAIKOF.

WHILE examining the eutectic alloys the author has observed that the alloy of copper and antimony corresponding to the second eutectic-point (69 per cent Cu) has a structure which depends on the rapidity of cooling, which leads to the belief that this compound has the property of undergoing, through tempering, modifications analogous to those of steel; with the object of deciding this point he undertook as complete an examination as possible of the alloys of copper and antimony.

Having determined the curve of fusibility of these alloys, Le Chatelier recognised the existence of a definite compound, $SbCu_2$, which was also confirmed by the metallographic work of Charpy; Stead admits the existence of the definite compound $SbCu_3$; it is the existence of this latter compound which it is necessary first to verify. For this purpose the author has examined the fusibility of the alloys of copper and antimony and their micro-structure, and under his direction M. Solovief has measured their hardness and their electromotive force.

The temperatures were measured by means of the Le Chatelier pyrometer. The fusion-point was determined by the observation of the speed of cooling of the fused alloys; the indications of the pyrometer were noted at stated intervals, determined by the beating of a metronome, or by the use of the recording apparatus devised by the late Sir Wm. Roberts-Austen. The alloys were prepared by melting together the two metals in the desired proportions; the composition did not vary by more than 0.5 per cent on account of the oxidation and volatility of the antimony, and the error in the measurement of the temperature hardly exceeded 2 or 3 degrees.

The curve of fusion-points showed a maximum (681°) for 61 per cent of copper; that is to say, the compound $SbCu_3$. On both sides of this point the curve falls away; that is to say, that an excess of either copper or antimony increases the fusibility; this portion of the curve corresponds to the separation of $SbCu$ as a solid phase. By increasing the proportion of copper, we find a eutectic-point (628°) corresponding to 69 per cent of copper; from this point the curve rises up to the fusing-point of copper. With a proportion of copper less than $SbCu_3$ there is another definite compound; we observe a transition-point corresponding to 40 per cent of copper; the proportion of copper in the definite compound thus satisfies the inequalities, 40 per cent $< x < 61$ per cent. On the other hand, the most simple formulae which can satisfy these conditions are:— Sb_2Cu_3 (44 per cent of Cu), $SbCu_2$ (54 per cent), and Sb_2Cu_5 (57 per cent). To decide which of these formulae expresses the definite compound the progress of the cooling must be examined.

The cooling of the alloys from 61 per cent to 51 per cent of Cu showed a retardation at a temperature variable with the composition; those from 54 per cent to 51 per cent of Cu show two retardations, one variable and the other fixed at 586°; those from 51 to 40 per cent show three retardations, one variable and two fixed at 586° and 524°. The

* Resorcin and β -naphthol, without any mixture of diphenylamine, were suggested by the author of the present note as reagents for nitrites, nitrates, and chlorates in the year 1897. (See the account given in *Comptes Rendus*, cxviii., No. 6; *Gazz. Chim. Ital.*, 1897, cxviii.; *CHEMICAL NEWS*, lxxix., No. 1992).

signification of these retardations of cooling is the following:—

The temperature 586° corresponds with a transition-point below which the compound of Sb and Cu is transformed into another one; it is at this temperature that equilibrium can exist between two solid phases, a liquid phase and the gaseous phase; and this point does not depend upon the proportions of Cu and Sb. The second fixed retardation point, 524° , is the fusing-point of the eutectic mixture of the compound α and of Sb. This retardation at 524° is no longer observed when we arrive at 51 per cent of Cu; at this point there is no longer any excess of antimony; the compound α thus contains 51 per cent of copper; that is to say, it corresponds to the formula SbCu_2 . It forms beautiful violet crystals.

The variable retardation of temperature of the alloys from 54 to 69 per cent of copper indicates the formation of solid solutions of mixed crystals of SbCu_3 , containing, according to circumstances, a more or less great excess of antimony or copper.

Thus the fusibility shows the existence of two definite compounds, SbCu_2 and SbCu_3 . The former is violet and the latter is white with a greenish appearance by reflected light; the alloys containing less than 51 per cent of copper have a shadowy violet appearance, which becomes less distinct as the proportion of copper decreases; the yellow tint only appears with alloys containing more than 70 per cent of copper.

The relative hardness of the alloys was measured by means of a sclerometer formed of a conical diamond loaded with a definite weight, the point of the diamond being thus pressed against the metal under examination; by means of a screw the diamond could be moved horizontally, leaving a scratch; this scratch was photographed by means of a metallographic microscope giving an enlargement of 150 times; thus the width of the mark could be measured. The results, represented by a curve of which the abscissae show the composition of the alloy and the ordinates the width of the scratch, show a maximum of hardness at about 58 per cent of copper; that is to say, at almost SbCu_3 . The compound SbCu_2 is shown distinctly by a change of direction in the curve of hardness.

The method of electromotive forces gives evidence of the existence of SbCu_2 , but it is easy to understand that it gives no indication as to SbCu_3 . It consists in measuring the tension of polarisation of two electrodes, one of Sb, the other of the alloy Sb and Cu, plunged into a solution of SbCl_3 in HCl, a constant current being kept passing from the alloy to the antimony through the electrolyte.

Besides the retardations in the speed of cooling due to solidification, there is one which occurs after the whole mass has solidified; sometimes we even observe an elevation of temperature, a recalcence of more than 20 degrees; these phenomena indicate that transformations occur in the solid state with the production of heat; the author has examined this very completely. The most important results are the following:—

The compound SbCu_3 (61 per cent of Cu) is polymorphous, the β -modification crystallises on the solidification of the alloy; it is stable up to a temperature of 407° ; at this temperature it is transformed into the α -modification, giving off 2.5 cal. per grm. of substance. The β -modification forms solid solutions of mixed crystals with Sb, of which the composition varies from 61 to 53.5 per cent of copper.

The α variety cannot dissolve Sb; this is why the mixed crystals of β are decomposed into $\text{SbCu}_3 \alpha$ and SbCu_2 . The transformation of $\text{SbCu}_3 \beta$ into $\text{SbCu}_3 \alpha$ at 407° is analogous to that of prismatic sulphur into the octahedric variety, but it takes place more rapidly; to preserve $\text{SbCu}_3 \beta$ at the ordinary temperature, it is necessary, when the alloy is solidified at about 600° , to cool it rapidly by plunging it into water. The density of β is 8.51 and that of α is 8.68.

The solid solutions containing 53.5 per cent of copper

(12.50 per cent of Sb and 87.5 per cent of SbCu_3 , or 77 per cent of SbCu_2 and 23 per cent of SbCu_3) at the temperature of their separation from the liquid phase (586°), are not yet saturated with regard to Sb, but are with regard to SbCu_2 , and on cooling SbCu_2 separates from the solid solution.

The existence of the compounds SbCu_2 and SbCu_3 capable of forming with Sb and Cu mixed crystals of solid solutions between certain limits of composition, the physical and chemical changes depending on the composition and the temperature, introduces a considerable complication, in spite of which the author has been able to arrive at the correct meaning of the phenomena observed. All these conclusions have been verified by the examination of the microstructure.—*Journ. Soc. Phys. Chim. R.*, vol. xxxvi., p. 111.

THE IMPORTANCE OF ACCURATE MEASUREMENTS AT VERY LOW TEMPERATURES.*

By Dr. H. KAMERLINGH ONNES.

(Continued from p. 150).

LET us turn our eyes from the wide field left to be explored by the pioneers to the tract that has already been conquered, and let us ask what we may expect from its cultivation.

We can best judge of this by means of a very important law discovered by Van der Waals in 1881, which formulates precisely various regularities in the behaviours of several substances, and brings them under a common point of view—the law of corresponding states. Let us therefore call to mind the properties of a substance in different conditions. If the temperature and the volume of a certain weight of a homogeneous substance are given (for convenience, we shall always consider a quantity proportional to the molecular weight), then the state of that substance is determined; a definite pressure, for instance, exists at which it will occupy that volume. Between that pressure, volume, and temperature a relation exists—the equation of state—in the same way as on a map in relief of a mountain there is a relation between the height of each place, its length, and its breadth. Each substance has its own equation of state, and hence, if we give it a tangible form, its own model, where, for instance, the height represents pressure, the length volume, and the breadth absolute temperature. Of the imaginary model of each substance, we know from experiments only that part which is contained within the usually relatively small range of temperature and pressure covered by our researches.

On the strength of the experience that the known parts of those models resemble each other a little, we can, by means of what we have actually observed on the one, form an idea of what we shall find on the other; in particular, we shall find on all these models, on one more to the front than on the other, a place which corresponds with the critical state. Moreover, the distance of the boiling-point from the critical-point is for all models about the same fraction of the critical temperature.

According to Van der Waals, however, the agreement between the equations of state of several substances goes much further. All their models bear a certain relation to the same fundamental model. To express this property we must construct the different models, each according to a different measure, *i.e.*, we must take the dimensions in the direction of the pressure according to the measure of the critical pressure, the dimensions in the direction of the volume according to that of the critical volume, and, lastly, the dimensions in the direction of the temperature according to the measure of the critical temperature.

* Address delivered in commemoration of the 329th Anniversary of the University of Leiden. From *Communications from the Physical Laboratory at the University of Leiden*, Suppl. No. 9 to No. 85—96.

In this manner we obtain for each substance its reduced model; on this reduced model the altitude of a point is called the reduced pressure, its longitude the reduced volume, and its latitude the reduced temperature. According to the law of corresponding states, all reduced models are identical. The law is not, however, valid for all substances; those which satisfy it are called *normal*. Nor does the law hold rigidly for these either; all reduced models do not coincide precisely with the one definite fundamental model; at the same reduced temperature and the same reduced volume—or, in other words, in states which are called *corresponding*—we do not observe, for instance, exactly the same reduced pressure. But the differences between the reduced models among themselves and between the same fundamental model are only slight.

If the law held rigidly, we might advance very far towards acquiring a survey of the whole equation of state merely by means of observations taken at ordinary temperatures only. The portions of the single models known to us from those observations we generally find back on the different reduced models at different places. For the critical temperature generally differs for different substances, and the temperature of observation must be divided by it to find the reduced temperature. Hence we would have only to combine the reduced portions found for normal substances of the most varied volatility in order to survey a very extensive part of the equation of state (*cf. Communications from the Physical Laboratory at the University of Leiden*, Nos. 71 and 74). These surveys have a great value. We need only call to mind the importance of the survey which Andrews has given first of all of the neighbourhood round the critical state for Van der Waals' theory.

In the treatment of the equation of state, questions arise which absolutely demand a survey of the largest possible range of reduced temperatures—a survey of a range as great as that covered by the model which we should get if we combined different portions derived from the investigations of different substances. Yet this model, which shows a certain average resemblance with the reduced models of all substances, but does not coincide exactly with any of them, proves quite unsatisfactory when we occupy ourselves with the questions considered here.

There are found all sorts of approximate relations for the equation of state and the quantities derived from it, which can be tested only by a survey of the same real model. The simplest instance is the thesis that in each model the sections for the same volumes are straight lines.

Are these sections indeed straight, or are they curved? The question cannot be properly answered by means of the model produced by combining different portions deduced from different substances. For as the slopes of the combined portions on different models need not be exactly the same, the combination of portions derived from several models with different directions may call forth the idea of a curvature, although on each of the reduced models the said sections were straight lines however far they were produced.

For Van der Waals' theory the solution of problems like this is of fundamental importance. Investigations of the different models wherever we think most convenient cannot lead us to our goal. The form of the model of one substance must, however much exertion it may cost, be investigated as completely as possible, as well at high as at low reduced temperatures.

Accurate measurements at high values of reduced temperature are feasible only with the permanent gases, and best of all with hydrogen, just because its critical temperature is so low, and hence the scale with which we measure is comparatively so subtle.

In order to work with carbon dioxide at the same reduced temperatures as those reached by Amagat with hydrogen, we should have to bring the carbon dioxide to more than 4000° C. Far below this temperature it is decomposed. But even if this were not the case, it would be as impossible to enclose this substance within walls at that high

temperature as it would be to enclose any other. Carbon dioxide cannot even be brought to the reduced temperatures to which, for instance, Amagat's measurements of oxygen and nitrogen extend.

All other substances except the permanent gases behave in this respect like carbon dioxide. The only means to gain a true understanding of the equation of state is to investigate the permanent gases at low temperatures in the same way as the less volatile substances are investigated at the ordinary temperatures. (Investigations related to this subject are treated in *Communications from the Physical Laboratory at the University of Leiden*, Nos. 69, 78, 84).

For the present it is not hydrogen, but the other so-called permanent gases which seem fit above all to give us a better knowledge of the equation of state over the largest possible range. Although by means of hydrogen a larger range may be covered, the difficulties attending the investigations of hydrogen at the lowest temperatures are still too great. As, however, the possibility to make this research exists, as its importance is beyond any doubt, and as, by means of this substance, owing to its very low critical pressure, higher reduced pressures can be attained than by any other, we cannot but learn in time to clear away the impediments of this investigation.

To have made this research possible, and, generally speaking, to have reduced by many times the attainable distance to the absolute zero, and thus to have increased by as many times the range of the available reduced temperatures, is the great scientific significance of Dewar's triumph.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, March 15th, 1905.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

MESSRS. A. G. Levy, F. L. Pyman, G. W. Monier-Williams, and W. H. Woodcock were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frank Standish Findon, M.A., B.Sc., 41, Great Percy Street, Holford Square, W.C.; Edwin Morris, 12, Dragon View, Harrogate; Frank Sheddin, B.Sc., 5, Belvedere road, Walsall; George Devenish Thomas, B.Sc., 8, Hubert Terrace, Dover.

The PRESIDENT announced that Prof. Percy Frankland had presented to the Society the eudiometer made and used by the late Sir Edward Frankland for the analysis of ethyl in 1849; that Prof. Retzius, of Stockholm, had presented an engraving of Berzelius; and that Mr. Oscar Guttmann had presented a bronze medal struck in honour of Roger Bacon in Paris in 1818. The Council, on behalf of the Society, had expressed their thanks for these gifts.

Of the following papers, those marked * were read:—

*36. "The Velocity of Oxime Formation in certain Ketones." By ALFRED WALTER STEWART.

With the object of gaining confirmation of the results already obtained in the case of the addition of sodium hydrogen sulphite to various ketones (*Proc.*, vol. xxi., p. 13), the author has investigated the rates of formation of the corresponding series of oximes. Solutions of the ketones were allowed to interact with a hydroxylamine sulphate solution for a fixed time, and the amount of free hydroxylamine was then estimated by warming with iodine solution and sodium phosphate and titrating with standard thiosulphate. The principal results are shown in the following table:—

Percentage of oxime.

	After 10	20	30 minutes.
Acetone.. .. .	45.1	49.7	50.0
Methyl ethyl ketone ..	36.6	39.2	39.2
Methyl isopropyl ketone ..	31.4	31.5	32.0
Pinacol	12.9	17.0	24.5

The results are generally in agreement with those already found for the addition of sodium hydrogen sulphite to ketonic compounds, and since chemically the two reactions belong to different types, it seems probable that the hindrance to the reactions in the case of ketones containing many methyl groups near the carbonyl is due to stereochemical and not to purely chemical causes.

*37. "The Ultra-violet Absorption Spectra of certain Enol-ketotautomerides." Part II. By EDWARD CHARLES CYRIL BALY and CECIL HENRY DESCH.

In the first part of this investigation (*Trans.*, 1904, lxxxv., 1029), the ultra-violet absorption spectra of acetylacetone and ethyl acetoacetate and of certain of their derivatives were described. Evidence was then brought forward in support of the view that the absorption band exhibited by these substances is due to the equilibrium existing between the two possible tautomeric forms. Neither of the two modifications when in a pure state gives an absorption band, but when the two are present together in mutual equilibrium, that is to say, when a number of molecules are changing from one form into the other, a very decided absorption band is developed. The oscillation frequency of the light absorbed was further shown to be independent of the mass of the atom in the so-called labile condition. The conclusions drawn in the first paper are now shown to be fully confirmed by an investigation into the absorption spectra of benzoylacetone, ethyl benzoylacetate, ethyl acetylsuccinate, ethyl diacetylsuccinate, ethyl oxaloacetate, ethyl acetonedicarboxylate, and ethyl benzoylsuccinate, together with certain of their derivatives. These results favour the view that the absorption band is due to the change of linking taking place when one tautomeric form passes into the other. It is possible to account for the formation of the absorption band by adopting the physical conception of the atoms as a system of electrons, and in this way the formation of the bands is placed in the same category as other spectral phenomena.

Some light is thrown on the dissociation of salts in solution by these results, and it appears probable that dissolved salts are not dissociated into independent ions, but that the two parts of the molecule are merely drawn apart to a certain extent by the action of the solvent. When the two parts are sufficiently separated to allow of the interchange of parts between adjacent molecules, then the condition known as ionisation exists. It is possible to have degrees of dissociation without any evidence such as is required by the electrolytic dissociation hypothesis; such degrees of dissociation no doubt occur in the case of organic compounds, which react apparently by means of ions, but the solutions of which present no evidences of the presence of the ions.

The aliphatic tautomeric compounds in solution present also a type of dissociation without the presence of ions. The labile atom is only drawn away from the rest of the molecule sufficiently to allow an interchange to occur between two different parts of the same molecule. The labile atom is a potential ion. Four grades of dissociation may be recognised.

DISCUSSION.

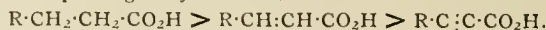
Sir W. RAMSAY remarked that the late Prof. Fitzgerald used to contend that the positive and negative ions could not be regarded as entirely independent entities, but must have some physical connection with each other. The "Faraday" tubes spoken of by Mr. Baly may be taken as such a connection. If it be asked how far it is possible to stretch a "Faraday" tube, when one atom, positively charged, may be taken as independent of a negatively charged atom with which it was originally in union, the answer is

that the atoms, formerly partners, may be separated by air, glass, or any material. Thus if an experiment suggested by Prof. Ostwald be conceived, in which the + and - ions of a solution of potassium chloride are present in different vessels, physicists would contend that the "Faraday" tube joining them would exist however far the ions be removed one from the other.

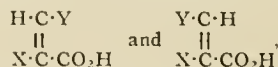
*38. "Esterification Constants of Substituted Acrylic Acids." By JOHN JOSEPH SUDBOROUGH and DAVID JAMES ROBERTS.

The esterification constants of some 22 substituted acrylic and allied acids with methyl alcohol have been determined at 15°. The following compounds were examined:—Crotonic, cinnamic, *allo*cinnamic, β -chloro-crotonic, β -chloro*s*crotonic, α -chlorocrotonic, methyl hydrogen fumarate, methyl hydrogen maleate, atropic, α -phenylcinnamic, α -phenyl*allo*cinnamic, α -bromocinnamic, α -bromo*allo*cinnamic, β -bromocinnamic, β -bromo*allo*cinnamic, α -chlorocinnamic, α -chloro*allo*cinnamic, β -chlorocinnamic, β -chloro*allo*cinnamic, furfurylacrylic, and *allo*furfurylacrylic, *n*-butyric, hydrocinnamic, and phenylpropionic acids.

The results indicate that a substituted acrylic acid is esterified much less readily than the corresponding saturated acid, and somewhat more readily than the corresponding acetylenic acid,—

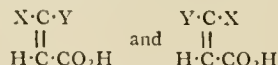


The effect of introducing substituents into acrylic acid is to lower the rate of esterification. This effect is the most marked when the substituent is in the α -position with respect to carboxyl. A comparison of the constants for pairs of stereoisomeric acids, for example,—



shows that the acid with CO_2H and Y in *cis*-position is esterified much less readily than when these substituents are in the *trans*-position. A similar relationship appears to hold good for pairs of acids, $Y \cdot CH : CH \cdot CO_2H$, with the exception of cinnamic and *allo*-cinnamic acids, which have exactly the same esterification constant.

No general relationships have been established hitherto between the pairs of acids,—



*39. " α -Chlorocinnamic Acids." By JOHN JOSEPH SUDBOROUGH and THOMAS CAMPBELL JAMES.

The action of alkalis on cinnamic acid dichloride and its methyl ester has been studied. The product is a mixture of α -chloro- and α -chloro*allo*-cinnamic acids, and the relative amounts of the two vary but little with the temperature or with the alkali. Even when the acid dichloride is acted on at low temperatures, the amount of α -chloro- acid (m. p. 137°) is considerable, and is raised to only a very small extent by substituting the methyl ester for the acid dichloride. Cinnamic acid dichloride does not show the same tendency to eliminate carbon dioxide as was observed with the dibromide, and hence the amount of chlorocinnamene is practically nil unless the reaction proceeds at a high temperature.

The velocities with which α -bromo, α -chloro, α -bromo*allo*, and α -chloro*allo*-cinnamic acids are acted on by aqueous potassium hydroxide have been determined.

The methyl ester, chloride, amide, anilide, *p*-toluidide, and α -naphthalide of the α -chloro-acid, and the chloride and amide of the α -chloro*allo*-acid have been prepared.

Phenylpropionic acid may be prepared by heating the α -chloro-acid with 20 per cent aqueous caustic potash (2.5 mols.) at 100° for eight hours; the yield is about 50 per cent of the theoretical amount, as carbon dioxide is evolved and an oil formed.

*40. "Diortho-substituted Benzoic Acid. Part VI. Conversion of Methyl into Ethyl Esters." By JOHN JOSEPH SUDBOROUGH and THOMAS HUW DAVIES.

Purdie has shown that methyl esters of aliphatic acids are readily transformed into the corresponding ethyl esters by means of ethyl alcohol and a small amount of sodium or sodium ethoxide. The methyl esters of substituted benzoic acids can be transformed in a similar manner provided the two ortho-positions with respect to the carbomethoxy-group are not occupied. Thus, the methyl esters of *p*-nitro-, *m*-nitro-, 3:5-dinitro-, 3:5-dibromo-, 3:5-dibromo-4-amino-, and 3:4:5-tribromo-benzoic acids have been converted into the corresponding ethyl esters, and the ethyl esters of *m*-nitro-, *p*-nitro-, 3:5-dinitro-, *p*-bromo-, 3:5-dibromo-4-amino-, 3:4:5-tribromo-benzoic acids have been converted into the corresponding methyl esters by means of methyl alcohol and a small amount of sodium methoxide.

Methyl 2:6-dibromobenzoate, methyl 2:4:6-tribromobenzoate, methyl 2:4:6-trinitrobenzoate, and ethyl 2:4:6-tribromo-3-aminobenzoate could not be transformed in this way.

DISCUSSION.

Dr. CAIN said that he was rather of the opinion that in the *o*-substituted compounds described by the author a linking might occur between an oxygen and a bromine atom, the former becoming tetradic, and the latter triadic, thus hindering or even altogether preventing the formation of an additive compound.

*41. "Simple Method for the Estimation of Acetyl Groups." By JOHN JOSEPH SUDBOROUGH and WALTER THOMAS.

The acetyl derivative (0.5—1.0 grm.) is added to a 10 per cent solution of pure benzenesulphonic acid and the mixture subjected to steam distillation until the distillate is no longer acid. With *o*-acetyl derivatives, this usually takes one to two hours if the steam is passed through somewhat rapidly. The distillate is then neutralised by means of standard barium hydroxide, using phenolphthalein as indicator. Satisfactory results have been obtained with acetyl-*a*-naphthol, diacetylquinol, triacetylpyrogallol, hexa-acetylmannitol, and triacetylgallic acid.

n-Acetyl groups may be estimated in a similar manner, but the operation takes somewhat longer, especially in the case of mono- or di-acetyltribromoaniline, the retardation being due to the influence of the ortho-substituents. Good results have been obtained with acetanilide, mono-, and di-aceto-*o*-toluidines, the corresponding *p*-compounds, diacetyl-*ψ*-cumidine, and the acetyl derivatives of *a*- and *β*-naphthylamines.

It is essential that the benzenesulphonic acid should be pure. The purification is readily accomplished by dissolving the barium salt in hot water, blowing steam through the solution until the distillate is neutral, allowing the barium salt to crystallise, and decomposing it with the theoretical amount of sulphuric acid.

Naphthalene-*a*- and *β*-sulphonic acids may be used instead of the benzenesulphonic acid.

*42. "Gynocardin, a New Cyanogenetic Glucoside." By FREDERICK BELDING POWER and FREDERIC HERBERT LEES.

The cyanogenetic glucoside *gynocardin*, the isolation of which from the seeds of *Gynocardia odorata* (R. Br.) has previously been recorded (Power and Gornall, *Proc.*, 1904, xx., 137) has now been further studied by the present authors.

Gynocardia seeds in contact with water afforded an amount of hydrogen cyanide equivalent to 0.44 per cent of the entire seed or 0.63 per cent of the kernels. The yield of crystalline glucoside was about 5 per cent of the weight of the seeds.

Gynocardin separates from water in colourless, glistening, prismatic needles containing 11H₂O, which it loses at 115°. The anhydrous substance has the formula C₁₃H₁₉O₉N, melts at 162—163°, and has $[\alpha]_D^{21} + 72.5^\circ$ in aqueous solution.

Hepta-acetylgynocardin, C₁₃H₁₂O₉(C₂H₃O)₇N, forms needles melting at 118—119°, and having $[\alpha]_D^{21} + 40.4^\circ$ in chloroform.

Gynocardin is readily hydrolysed at the ordinary temperature by *gynocardase*, the enzyme isolated from the seeds, but with difficulty by boiling 5 per cent hydrochloric or sulphuric acid, according to the equation:—
C₁₃H₁₉O₉N + H₂O = C₆H₁₂O₆ + C₆H₁₃O₄ + HCN.

Among the products of hydrolysis by either acids or the enzyme, it has been possible to isolate only *d*-glucose and hydrogen cyanide, the third substance, C₆H₁₃O₄, readily undergoing secondary decomposition with the formation of amorphous matter. By its comparatively great stability towards acid hydrolysing agents, gynocardin differs in a marked manner from the four other known members of its class (compare Dunstan and Henry, *Phil. Trans.*, 1901, cxiv., 515; 1902, cxix., 399; *Proc. Roy. Soc.*, 1903, lxxii., 285).

Gynocardin is readily hydrolysed by barium hydroxide with the formation of crystalline *barium gynocardate*, (C₁₂H₁₉O₉·CO₂)₂Ba, and ammonia, according to the equation:—
C₁₃H₁₉O₉N + 2H₂O = C₁₂H₁₉O₉·CO₂H + NH₃.

Gynocardic acid, C₁₂H₁₉O₉·CO₂H, forms a syrup which does not reduce Fehling's solution, and is dextro-rotatory; it is hydrolysed by acids in accordance with the equation:—
C₁₂H₁₉O₉·CO₂H + H₂O = C₆H₁₂O₆ + C₇H₁₁O₆.

d-Glucose and an *acid* are thus formed. The latter could be isolated in the form of its *quinine salt*, C₂₀H₂₄O₂N₂·C₇H₁₁O₆, which crystallised in needles melting at 224° with decomposition. This salt, however, could only be separated in such small amount from the sugar which accompanied it that it has been impossible to determine the constitution of the acid C₇H₁₁O₆.

The foregoing results point, however, to the conclusion that gynocardin is the *d*-glucose ether of the cyanohydrin of either a trihydroxyaldehyde, C₅H₄(OH)₃·CHO, or a ketone, C₅H₅(OH)₃·CO, respectively. In accordance with this view, the constitution of gynocardin can be represented by one of the following formulae: C₅H₄(OH)₃·CH(CN)·O·C₆H₁₁O₅ or C₅H₅(OH)₃·C(CN)·O·C₆H₁₁O₅.

Gynocardin is devoid of any appreciable physiological action.

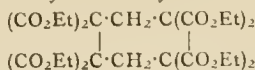
43. "Catechin and Acacatechin." (Supplementary note). By ARTHUR GEORGE PERKIN.

As previously found, catechin (from Gambier catechu), when dried at 100°, melts at 175—177°, and Clausen's statement (*Ber.*, 1903, xxxvi., 101) that anhydrous catechin melts at 210° could not be substantiated. Acacatechin, C₁₅H₁₄O₆·3H₂O, dried over sulphuric acid, loses 11H₂O, and differs from catechin, C₁₅H₁₄O₆·4H₂O, which under these conditions evolves 3H₂O. *Acacatechin tetramethyl ether* yields the acetyl compound, C₁₅H₇O₆(CH₃)₄·C₂H₃O (colourless needles, m. p. 135—137°), and on oxidation with potassium permanganate gives *veratric acid* and another substance, which is probably *phloroglucinol dimethyl ether*. Catechin tetramethyl ether behaves similarly. With sulphuric or hydrochloric acid in the presence of acetic acid, catechin and acacatechin give an orange-red anhydride having the same composition in both cases (C = 63.26; H = 3.89; and C = 63.33; H = 3.94 respectively), which is insoluble in alkaline solutions and the usual solvents, but which is not identical with the "catechuratin" of Kraut and Delden (*Annalen*, 1863, cxxviii., 270) and Etti (*Annalen*, 1887, clxxvi., 332). When oxidised with potassium ferricyanide in the presence of an alkali acetate, both catechins yield a new colouring matter, which dyes mordanted fabrics in orange-brown shades.

44. "The Action of Ethyl Dibromopropanetetracarboxylate on the Disodium Derivative of Ethyl Propanetetracarboxylate." (A correction). By WILLIAM HENRY PERKIN, jun.

A short time ago (*Trans.*, 1903, lxxxiii., 780), T. W. D. Gregory and the author published the results of a research

on the above decomposition, and stated that the product of the reaction was *ethyl hexamethylenecarboxylate*.—



Dr. Max Guthzeit has called the attention of the present author to the fact that this interpretation is incorrect, and that the substance actually formed is *ethyl trimethylenetetracarboxylate*.—

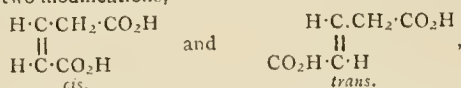


The substances described by Gregory and Perkin as hexamethylene derivatives are therefore in reality trimethylene compounds.

This remarkable formation of the trimethylene ring is discussed in the detailed paper.

45. "*Glutaconic Acid and the Conversion of Glutaric Acid into Trimethylenedicarboxylic Acid*." By WILLIAM HENRY PERKIN, jun., and GEORGE TATTERSALL.

Glutaconic acid has hitherto only been obtained in one modification, although stereochemical theory indicates that the two modifications,—



corresponding with fumaric and maleic acids, should exist.

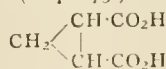
Ordinary glutaconic acid (m. p. 134°) is the *cis*-modification, since it yields an anhydride which, under reduced pressure, distils without decomposition, and on hydrolysis yields the same acid (compare Buchner, *Ber.*, 1890, xxiii., 706).

The authors have been engaged in a series of investigations with the object of preparing the unknown or *trans*-modification of glutaconic acid, but without success.

When glutaconic acid is distilled, it decomposes partially into vinylacetic acid, $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, and carbon dioxide, but when heated with water at 180°, the decomposition takes place in another direction, and crotonic acid (m. p. 72°) results.

β-Hydroxyglutaric acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, on distillation, yields a mixture of *cis*-glutaconic acid and its anhydride, and, when treated successively with phosphorus pentachloride and alcohol, it is converted into *ethyl β-chloroglutarate*, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, which, when digested with diethylaniline and subsequently hydrolysed, regenerates *cis*-glutaconic acid.

Ethyl α-bromoglutarate, $\text{CO}_2\text{Et}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, is obtained from glutaric acid by bromination and subsequent esterification. When this ester is digested with diethylaniline and subsequently hydrolysed, or when simply hydrolysed with alcoholic potash, it yields *trans*-trimethylenedicarboxylic acid (m. p. 175°).—



(compare Bowtell and Perkin, *Proc.*, 1899, xv., 241). *Ethyl α-iodoglutarate*, obtained from the bromo-ester by digesting with potassium iodide, behaves in exactly the same manner.

46. "*The Transformations of Highly Substituted Nitroaminobenzenes*." By KENNEDY JOSEPH PREVITÉ ORTON and ALICE EMILY SMITH.

The *s*-trisubstituted nitroaminobenzenes do not undergo the isomeric change into nitroanilines characteristic of less substituted nitroaminobenzenes, since the ortho- and para-positions in the benzene nucleus relative to the amino-group are occupied. In some cases, for example, 1-nitroamino-*s*-tribromobenzene, a nitroaniline is produced by displacement of a bromine atom by the nitro-group under the same conditions in which the isomeric change is effected, namely, in acetic acid solution in the presence of sulphuric acid (*Trans.*, 1902, lxxxi., 490, 806). In other cases, a

more complex decomposition takes place. For example, *s*-trichloronitroaminobenzene, which is obtained from *s*-trichloroaniline, yields *s*-trichlorobenzenediazonium salt, ammonia, and *s*-trichlorophenylimino-2:3:6-trichlorobenzoquinone, $\text{C}_6\text{H}_2\text{Cl}_3\cdot\text{N}\cdot\text{C}_6\text{HCl}_3\cdot\text{O}$, the two latter being in molecular proportions. The iminoquinone crystallises from petroleum in red crystals melting at 143°; on reduction, it is converted into 2:4:6:2':3':6'-hexachloro-4-hydroxydiphenylamine, $\text{C}_6\text{H}_2\text{Cl}_3\cdot\text{NH}\cdot\text{C}_6\text{HCl}_3\cdot\text{OH}$, which crystallises in long colourless needles melting at 186°. When hydrolysed by sulphuric acid, the iminobenzoquinone is converted into molecular proportions of *s*-trichloroaniline and 2:3:6-trichlorobenzoquinone.

Since in all cases the acetic acid solutions of nitroaminobenzenes, on treatment with sulphuric acid, yield magenta, purple, or indigo-blue solutions from which are obtained on dilution nitroanilines or substituted phenyliminoquinones, according as the ortho- and para-positions with respect to the imino-group are occupied by other groups, it seems probable that analogous compounds, possibly quinone derivatives, are always present in these solutions; from these intermediary substances are produced, on the one hand, the nitroanilines, or, on the other, the iminoquinone derivatives.

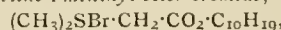
47. "*An Asymmetric Synthesis of Quadrivalent Sulphur*." By SAMUEL SMILES.

The *l*-menthyl ester of methylethylthetine bromide was prepared from *l*-menthyl bromoacetate and methyl ethyl sulphide. It was found that (a) the product yields an inactive methylethylthetine on saponification with silver oxide or with cold concentrated hydrochloric acid; (b) that the molecular rotatory power of the product lies nearly halfway between those of the dimethyl and diethyl derivatives, and that this relation is also shown by the corresponding platinichlorides; (c) that the platinichloride of *dl*-methylethylthetine *l*-menthyl ester bromide, when prepared from *l*-menthol and the acid bromide of *dl*-methylethylthetine, has the same rotatory power as the platinichloride made from the product of asymmetric synthesis.

Hence it is concluded that the two isomeric *d*- and *l*-methylethylthetine *l*-menthyl ester bromides are produced in equal amount from the interaction of methyl ethyl sulphide and *l*-menthyl bromoacetate.

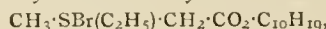
l-Menthyl bromoacetate, a colourless oil boiling at 144—145° 12 m.m., has a sp. gr. 1·208 at 25/4° and $[\alpha]_D^{25} - 61\cdot98^\circ$ and $[\text{M}]_D^{25} - 171\cdot68^\circ$; when dissolved in alcohol ($c = 12\cdot21$), $[\alpha]_D^{24}$ is $-62\cdot24^\circ$ and $[\text{M}]_D - 172\cdot4^\circ$.

Dimethylthetine l-menthyl ester bromide,—



melts at 87—90° with decomposition; in absolute alcohol, it has $[\text{M}]_D - 157\cdot9^\circ$, and in 50 per cent alcohol $[\text{M}]_D - 162\cdot7^\circ$, and in acetone solution $[\text{M}]_D - 159\cdot2^\circ$; the chloride has $[\text{M}]_D - 162\cdot0^\circ$ approximately; the hydroxide is an oil which slowly decomposes into menthol and dimethylthetine. The platinichloride melts at 177°, and in epichlorohydrin gives $[\text{M}]_D - 371\cdot3^\circ$.

dl-Methylethylthetine *l*-menthyl ester bromide,—



melts at 80—82°, and in alcoholic solution has $[\text{M}]_D - 162\cdot7^\circ$. Its platinichloride melts at 173—174°, and has $[\text{M}]_D - 351\cdot0^\circ$ in epichlorohydrin.

Diethylthetine l-menthyl ester bromide,—



melts at 73—74°, and has $[\text{M}]_D - 169\cdot0^\circ$ in alcoholic solution. The platinichloride melts at 148—149°, and a solution in epichlorohydrin gave $[\text{M}]_D - 331\cdot9^\circ$.

48. "*The Action of α-Halogen Ketones on Alkyl Sulphides*." By SAMUEL SMILES.

It has been found that certain α -halogen-substituted ketones interact with alkyl sulphides forming the halides of sulphine bases. The reaction is by no means general, for bromodiphenacyl, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_5$, α -bromocamphor, and certain other ketones do not act in

this manner. Further, the activity of the bromine cannot be entirely due to the proximity of an acid radicle to the CH_2Br group, for phenylbromomethylsulphone, $\text{CH}_2\text{Br}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_5$, is without action on the alkyl sulphides. This behaviour of the α -halogen ketones is interesting when compared with that of the α -halogen-substituted acids which also contain the group $\text{CH}_2\text{Br}\cdot\text{CO}$, and react in a similar manner.

Monochloroacetone and methyl sulphide yield *acetonyl-dimethylsulphine chloride*, $(\text{CH}_3)_2\text{SBr}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$, a colourless, uncrystallisable syrup which is very soluble in water; the *platinichloride* consists of pale yellow needles melting at $185-186^\circ$.

ω -Bromoacetophenone and methyl sulphide unite to give a theoretical yield of *dimethylphenacylsulphine bromide*, $(\text{CH}_3)_2\text{SBr}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_5$, which forms long colourless needles, melting at 148° ; it is soluble in hot water or alcohol, but very sparingly so in acetone. The *hydroxide* crystallises from chloroform in colourless leaflets which melt at $59-60^\circ$; it dissolves readily in water, giving strongly alkaline solutions. The *platinichloride* is thrown down from the aqueous solution of the chloride as a pale buff-coloured precipitate which, when pure, melts at $196-197^\circ$ with decomposition. On mixing saturated alcoholic solutions of picric acid and the bromide, the *picrate* is precipitated in sparingly soluble needles (m. p. $151-152^\circ$). The *dichromate* is insoluble in water, and melts at $168-169^\circ$.

Diethylphenacylsulphine bromide forms colourless needles (m. p. $88-89^\circ$) which are very soluble in water and alcohol, but sparingly so in acetone and ethyl acetate; the *platinichloride*, a pale buff-coloured powder insoluble in most organic media, melts at $146-147^\circ$ with decomposition. The *picrate* crystallises from hot alcohol in the form of bright yellow needles, and melts at $125-126^\circ$. *Diamylphenacylsulphine bromide* is a colourless crystalline substance which is soluble in water or alcohol, and melts at $60-61^\circ$; the *platinichloride*, melting at $138-139^\circ$, is soluble in warm ethyl acetate. Dimethyl sulphide and bromodecylbenzoin give *dimethyldecylsulphine bromide*, $(\text{CH}_3)_2\text{S}\cdot\text{CHBr}(\text{C}_6\text{H}_5)\cdot\text{CO}\cdot\text{C}_6\text{H}_5$; this substance crystallises from warm ethyl acetate in colourless prisms which melt and decompose at 110° ; the *platinichloride* dissolves in warm acetone, and crystallises therefrom in buff-coloured needles which melt at 162° ; the *picrate* forms yellow needles melting at 190° . (For other desyl derivatives, compare *Trans.*, 1900, lxxvii., 1178).

49. "Pinene iso.Nitrosocyanide and its Derivatives." By WILLIAM AUGUSTUS TILDEN and HARRY BURROWS.

A brief description of the cyanide and some of its reactions has been given in the "Preliminary Notice of some New Derivatives of Pinene and Other Terpenes" by the same authors (*Proc.*, 1902, xviii., 161).

Pinene isonitrosocyanide is shown to be a nitrile from which has been obtained, by the action of strong sulphuric acid, an amide of corresponding constitution. Pinene isonitrosocarboxylamide, $\text{C}_{10}\text{H}_{15}(\text{NOH})\cdot\text{CO}\cdot\text{NH}_2$, forms prisms which melt at 220° . It yields a methyl ether, which forms large colourless prisms melting at 145° and a benzoyl derivative melting at 197° .

Pinene isonitrosocarboxylic acid, corresponding with the amide, has not been obtained, but hydrolysis with hydrochloric acid yields an oily acid volatile in steam, which is probably the ketonic acid, $\text{O}\cdot\text{C}_{10}\text{H}_{15}\cdot\text{CO}_2\text{H}$.

By the continued action of sulphuric acid on the amide, an isomeric change is induced, the product having the properties of the lactam in which the oxime group, $\text{C}\cdot\text{N}\cdot\text{OH}$, has been converted into a carbonyl group, while an imino-group enters into the ring, thus, $-\text{CO}\cdot\text{NH}-$.

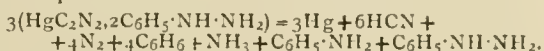
From this compound, by boiling with caustic potash, the corresponding acid has been obtained. The amide crystallises in prisms, which melt at 209° , and contain 1 molecule of water of crystallisation. The acid also contains water of crystallisation, and melts at 220° .

The silver and other salts of this acid have been prepared and analysed.

When heated with hydrochloric acid, the acid is converted into an amino-acid, which forms a stable crystalline hydrochloride. In the formation of this compound, it is believed that the ring is opened and, by the assumption of the elements of water, the group $-\text{CO}\cdot\text{NH}-$ is converted into $-\text{CO}_2\text{H}$ and NH_2- .

50. "Some Interactions of Metallic Cyanides with Organic Bases." By ROBERT DE JERSEY FLEMING STRUTHERS.

Phenylhydrazine heated with mercuric cyanide effervesces and deposits reduced mercury. This result might be indicated by the following obvious and simple equation: $-\text{HgC}_2\text{N}_2 + \text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{NH}_2 = \text{Hg} + 2\text{HCN} + \text{N}_2 + \text{C}_6\text{H}_6$, but in reality the reaction is complicated by the formation of the intermediate compound, $\text{HgC}_2\text{N}_2\cdot 2\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{NH}_2$. This substance is a white, lustrous, crystalline solid, sparingly soluble in water or alcohol; it melts and decomposes with effervescence at about 110° according to the equation:—



Phenylhydrazine, when heated with cuprous cyanide, effervesces, but in other respects the action is different from that which obtains in the case of the mercury compound. An intermediate compound, $\text{CuCN}\cdot\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{NH}_2$, was isolated in the form of brilliant scales with a silvery metallic lustre. This substance becomes rapidly discoloured at the ordinary temperature, evolves nitrogen, and ultimately acquires a deep coppery lustre. This evolution of gas was proved to be due not to spontaneous decomposition, but to an action of atmospheric oxygen.

When heated to a somewhat higher temperature than that required for the mercury salt, the copper derivative decomposes, thus:—



From the above reaction, it seemed possible that cuprous cyanide might exert a catalytic action on phenylhydrazine. This proved to be the case, quite a small quantity of the cyanide under proper conditions of temperature sufficing to liberate nearly the theoretical yield of nitrogen from a large excess of phenylhydrazine, the actual amount being some thirty times as much as would have been the case had there been no catalysis. The action is probably due to the alternate decomposition and regeneration of the compound $\text{CuCN}\cdot\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{NH}_2$.

The cyanides of mercury, copper, and silver were also found to form definite additive compounds with pyridine, aniline, quinoline, and other similar bases.

Complex Compounds of Copper.—V. Kohlschütter.

—A concentrated solution of NH_3 , treated with a cupric salt containing a slight excess of CNSK , gives dark blue plates of ammoniacal cupric thiocyanate, $\text{Cu}(\text{CNS})_2\cdot 4\text{NH}_3$, soluble in water with a violet colouration; if we add CNSK to the solution we obtain insoluble blue needles, $\text{Cu}(\text{CNS})_2\cdot 2\text{NH}_3$. On the addition of KI to a solution of iodide of cuprammonium, $\text{CuI}_2\cdot 4\text{NH}_3\cdot \text{H}_2\text{O}$, the violet liquid changes to green, and there are deposited large, almost black crystals of $3\text{CuI}_2\cdot 10\text{NH}_3$, or perhaps $2[\text{CuI}_2\cdot 3\text{NH}_3]\cdot \text{CuI}_3\cdot 4\text{NH}_3$. With oxalate of potassium we precipitate blue crystals of $\text{C}_2\text{O}_4\text{Cu}\cdot 2\text{NH}_3\cdot 6\text{H}_2\text{O}$. If we add $\text{C}_2\text{O}_4\text{K}_2$ to even a very ammoniacal solution of $\text{SO}_4\text{Cu}\cdot 4\text{NH}_3$, we precipitate beautiful blue prisms of ammoniacal cupric oxalate, $\text{C}_2\text{O}_4\text{Cu}\cdot 2\text{NH}_3\cdot 6\text{H}_2\text{O}$. The ammoniacal cupric bromide, $3\text{CuBr}_2\cdot 10\text{NH}_3$, is only obtained with heat; by the addition of KBr we obtain a greenish-blue basic salt, $\text{CuBr}_2\cdot 2\text{CuO}\cdot 2\text{NH}_3$. In the electrolysis of aqueous solutions of CuCl_2 , the cation appears to contain water, and we should have the following equilibrium: $—[\text{CuCl}(\text{H}_2\text{O})_3] + \text{H}_2\text{O} = [\text{Cu}(\text{H}_2\text{O})_4] + \text{Cl}$. The elevation of temperature favours the formation of the chlorised anion.—*Berichte*, vol. xxxvii., p. 1153.

NOTICES OF BOOKS.

Practical Methods of Electro-chemistry. By F. MOLLWO and J. PERKIN, Ph.D. With Frontispiece and 64 Illustrations in the Text. London, New York, and Bombay: Longmans, Green, and Co. 1905. Pp. 322.

ONE of the reasons given by the author for writing the present book is the hope that interest in electro-chemistry might be stimulated. The progress in electro-chemistry in recent years is little short of marvellous, not so much perhaps in the laboratory as in the factory; still it is in the laboratory that processes and results are planned and checked.

Well knowing the importance of the subject, the author has personally tested and supervised, as far as possible, all the experimental work included in the volume, and with few exceptions all this work has been carried out in the laboratories of the Borough Polytechnic Institute.

The book is divided into three principal parts. Part I., general, covers only 82 pages, and deals with the production and regulation of the current, instruments, apparatus, &c. In Part II. we come to electro-chemical analysis, metals deposited as oxides at the anode, and the separation of metals. This latter operation may be carried out by various means, such as (1) separation by variable potential, but this method is only applicable when the decomposition values do not lie too close together; (2) separation by depositing one metal on the cathode and the other on the anode as oxide; (3) separation by choice of electrolyte; for instance, some metals can only be deposited from strongly acid solutions, others from dilute acid, and others again from alkaline solutions; (4) the artificial alteration of decomposition values by the formation of complex salts; and (5) Hollard's methods, the first of which really comes under heading 4; in the second of these methods the anode and cathode are separated by a parchment or porous diaphragm. In the third method the influence of the nature of the cathode is made use of; thus by taking a cathode made of the same metal as that to be deposited, the polarisation potential of hydrogen is raised above the polarisation potential of the metal to be deposited, and such metals as lead, tin, and cadmium can be precipitated from strongly acid solutions.

Part III. is on preparations by electrolytic means, and deals with both organic and inorganic electrolysis, and the reduction and oxidation of organic compounds.

This is followed by a short account of the preparation of some of the reagents and materials necessary for carrying out the various operations described; there are also a few pages containing some useful data, and a table of five-figure logarithms, while the book is closed with a short index.

The Chemistry of Coke. Founded on the "Grundlagen der Koks-chemie" of O. SIMMERSBACH. Second Edition. Revised and Enlarged by W. CARRICK ANDERSON, M.A., D.Sc., &c. Glasgow and Edinburgh: William Hodge and Co. 1904. Pp. 201.

A good deal of additional matter has been included in this the second edition of the "Chemistry of Coke." Among these additions the author draws attention to a detailed description of methods for detecting minute quantities of arsenic in fuels, which have been devised in consequence of the arsenic scare of 1900.

These methods, of which the most important is Prof. Thorpe's, will be found on pages 166 to 183.

The book is divided into seven chapters, beginning with the purpose of coking and the uses of coke. The coking power of coal and the coking process form the subjects of Chapters II. and III., while the chemical composition of coke is dealt with in Chapter IV. Chapter V. is on the physical properties of coke; the important subject of the ability and calorific value of coke is fully gone into

in Chapter VI. We have already referred to Chapter VII., which is on the chemical and physical examination of coal and coke.

The book, though not large, is a useful one, and should be appreciated by works chemists and others who have to do with this subject. There is a short but efficient index.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxi., No. 10, March 6, 1905.

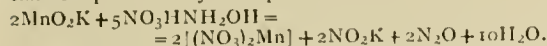
1-Methyl-4-benzylcyclohexanols and 1-Methyl-4-dibenzylcyclohexanol.—A. Haller and F. March.—The authors' researches show that, at a high temperature, methylcyclohexanone behaves to sodium alcohols differently from camphor. Camphor giving benzyl camphor when treated with sodium benzyllate, with a very small quantity of a viscous product; whilst methylcyclohexanone, under the same conditions, gives rise to a mixture of methylbenzyl and methylidibenzyl hexanols; that is to say, to the mono- and di-substituted derivatives of methylhexanol. During this reaction a substitution and a hydrogenation take place simultaneously, whilst, in the case of camphor, only a substitution takes place.

Time taken for Precipitation in Solutions of Hypo-sulphite.—Gaston Gaillard.—The author investigates the conditions which influence the time taken for the first appearance of opalescence in solutions of hyposulphite when these salts are precipitated by different reagents.

Electrolytic Solution of Platinum in Sulphuric Acid.—André Brochet and Joseph Petit.—The authors find that a current of varying intensity induces the solution of platinum in sulphuric acid. An alternating current has no specific action due to reversing the sense of the current, and the results observed with such a current correspond to the resultant of the anodic and cathodic phenomena. In the absence of an oxidising agent, the solution of the metal acting as anode, and due to the variation in intensity of the current, is counterbalanced exactly by the precipitation in the form of platinum black. The presence of an oxidising agent does not allow of the formation of a higher platinum oxide, nor does it favour solution; it simply prevents the normal reduction of the platinum salt, so that the metal remains in solution. Naturally, the concentration of the platinum in the solution is limited, and an equilibrium-point is attained which varies according to the conditions of the experiment. If, during the electrolysis of the sulphuric acid alone, a continuous current is added to the alternating current, solution occurs by an analogous process, and an amount of metal goes into solution, varying according to the anodic electricity resulting from the combined action of the two currents, and which would only be partially deposited by the single cathodic action of the alternating current. The absolute action of the alternating current is nil, and the continuous current of constant intensity behaves as if it were transformed into a continuous current of varying intensity.

Comparative Physical Properties of Pure Nickel and Cobalt.—H. Copaux.—The author prepares nickel and cobalt in a very pure form, and finds that they both contain 1/2000 to 1/4000 part of their weight of non-metals, estimated as a residue when the metal is dissolved in copper and potassium chloride. The metals are both magnetic, very crystalline, and non-malleable when cold. They are different enough in appearance to be distinguished at a glance—cobalt being brilliant silvery white, whilst nickel is dull and greasy.

Action of Potassium Permanganate on Hydroxylamine Salts (Nitrate, Phosphate, Arseniate).—L. J. Simon.—When a decinormal solution of permanganate acts on a neutral solution of hydroxylamine nitrate, the permanganate is decolorised; a brown precipitate of manganese oxide is deposited, which can be re-dissolved by shaking. After a certain quantity of permanganate solution has been added the precipitate ceases to dissolve, and gives the liquid a faint yellowish tinge, easy to detect. The oxidation of the hydroxylamine is then complete, and can be represented by the equation—



Quadrivalent Oxygen.—E. E. Blaise.—The author's present research shows that the mono-, di-, and trioxyc compounds (ether oxides, acetals, ortho-ethers, &c.), give iodo-magnesium compounds of the same type containing 1 molecule of magnesium iodide to 2 molecules of the oxy-compound. All such compounds react in an analogous way on benzoyl chloride, and the observed reactions demonstrate the intimate union of the mineral and the organic molecule by the intermediary of an atom of quadrivalent oxygen. In the case of the ether salts, the iodo-magnesium compound corresponds to a different type, $(\text{CH}_3-\text{CO}_2\text{C}_2\text{H}_5)_6\text{MgI}_2$.

Decomposition of *o*-Nitrobenzyl Alcohol under the Influence of Aqueous Soda and Alcoholic Soda.—P. Carré.—Under the influence of aqueous soda, the group NO_2 of *o*-nitrobenzyl alcohol is reduced at the expense of the alcohol group, which disappears completely, being transformed into the acid group or into the aldehyde group, whilst, under the influence of the alcoholic soda, the reduction of the NO_2 group is effected, partially by the alcohol introduced and partially by the *o*-nitrobenzyl alcohol. There exist, therefore, alcoholic and indazyl compounds which can effect the dehydration of azoic alcohols, as M. Freundler has previously proved. Sodium ethylate acts in an analogous way to alcoholic soda, with the small difference that the proportion of the unchanged alcohol group is slightly higher. Finally, the relative quantities of the products formed vary with the quantity of soda in the aqueous or alcoholic solution.

Bulletin de la Société Chimique de Paris,
Series 3, vol. xxxi., No. 10.

Preparation and Properties of Cæsium-ammonium and of Rubidium-ammonium.—Henri Moissan.—Already noticed.

Action of Acetylene on Cæsium-ammonium and on Rubidium-ammonium. Preparation and Properties of the Acetylenic Acetylides, $\text{C}_2\text{Cs}_2\cdot\text{C}_2\text{H}_2$, $\text{C}_2\text{Rb}_2\cdot\text{C}_2\text{H}_2$, and of the Carbides of Cæsium and Rubidium.—Henri Moissan.—Already noticed.

Preparation of Carbides and Acetylenic Acetylides by the Action of Acetylene Gas on the Alkaline and Alkaline-earth Hydrides.—Henri Moissan.—Already noticed.

Preparation and Properties of Silicide of Ruthenium.—Henri Moissan and Wilhelm Manchot.—Already noticed.

Double Carbide of Chromium and Tungsten.—Henri Moissan and A. Kousnetzow.—Already noticed.

Action of Carbonic Anhydride on the Ammonium Metals.—Etienne Rengade.—Already noticed.

Arsenide of Cadmium.—Albert Granger.—Already noticed.

New Method for the Fractionation of Ceric Earths.—H. Lacombe.—Already inserted in full.

"Colloidal Silvers."—M. Hanriot.—A controversial paper, not suitable for abstraction.

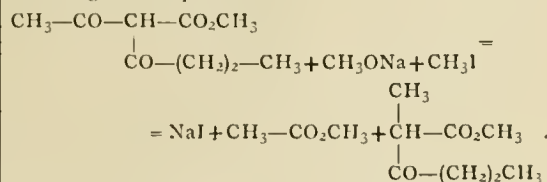
Determination of the Calorific Power of Blast-furnace Gases by means of the Calorimetric Bomb.—G. Arth.—The author expresses the opinion that, although M. Mahler's calorimetric bomb is an excellent apparatus for the determination of the calorific power of solid and liquid fuels, the same is no longer the case when we have to do with poor gases, such as those which escape from blast furnaces, and he gives his reasons in full for this opinion, and thinks that equally good or better results can be calculated from an ordinary analysis.

Estimation of Nitrogen.—Léon Débourdeaux.—Already noticed.

Estimation of Chlorides in Urine.—J. Ville and E. Derrien.—The authors compare several known methods for the estimation of chlorides in urine, such as that of Mohr, Charpentier, Denigès, Loubiou, Freund-Topler, and the direct process. They consider the Charpentier method as one of the most exact.

General Method for the Synthesis of Aldehydes.—F. Bodroux.—Already noticed.

General Method for the Preparation of Acylacetic and Substituted Ethers.—M. Bouveault and R. Locquin.—The necessary quantity (1 molecule) of alcoholate of sodium is prepared, taking care to use as the alcohol one in which the radical is in the ether group of the molecule, so as to avoid substitutions. This alcoholate of sodium is added gradually to the corresponding quantity of C-acetylacetic ether under treatment, avoiding too high a temperature. The cold solution is left in a stoppered flask for twelve hours; we then add an alcoholic iodide and heat to $100-110^\circ$ for six hours. After cooling, we must make sure that the product is neutral or slightly acid. The alcohol is then driven off by distillation, and the residue taken up with water, extracted with ether, washed with a solution of carbonate of soda and hyposulphite if necessary, the ether driven off, and the residue rectified *in vacuo*. The non-saturated carbide distils over first, then the non-substituted acetylacetic ether, then an intermediate portion containing the α -substituted acetylacetic ether and the non-substituted acylacetic ether. Finally, almost without leaving any residue, the desired product comes over according to the equation—



Some Homologues of the Butyryl- and Isovalerylacetic Ethers.—René Locquin.—By the application of the general method for the preparation of the acylacetic ether described in the previous paper, the author has obtained four derivatives by treating C-butyrylacetylacetate of ethyl with iodide of ethyl in alcoholate of sodium. The first is the ethylbutyrylacetylacetate of ethyl; the second, propylbutyrylacetylacetate of ethyl; the third, isopropylbutyrylacetylacetate of ethyl; and the fourth, capryl(secondary)-butyrylacetylacetate of ethyl.

Some Homologues of Caproyl- and Isocaproylacetic Ethers.—René Locquin.—Like their homologues, these new β -ketonic ethers have been obtained by the application of the method described above. In this paper the author describes the preparation and properties of some derivatives of C-caproylacetylacetate of ethyl, and of C-isocaproyl(natural)-acetylacetate of ethyl.

Synthetic Isoamylic Alcohol and Commercial Amylic Alcohol.—René Locquin.—The author shows that the differences between the derivatives of ordinary isoamylic alcohol and synthetic isoamylic alcohol are enormous; it is necessary, therefore, to specify always which substance has been used.

Mannamine: a New Base derived from Mannose.—E. Roux.—Already noticed.

Dibromised Ethylcarbylamine.—H. Guillemaud.—When bromine and a small quantity of ethylcarbylamine are brought together in the presence of water, the mixture becomes heated, cloudy, and is finally decolourised; on evaporation, it deposits a small quantity of a crystalline body. To examine this reaction more closely, the author placed a layer of ethylcarbylamine over distilled water through which a current of air charged with bromine was passed. Under these conditions, the layer of carbylamine disappeared, while a very dense oily liquid was formed, only to disappear in its turn, giving off bubbles of gas. When evaporated on the water-bath, the liquid gave off a considerable quantity of HBr , and left a crystalline residue, which, after purification, was shown to consist of bromhydrate of ethylamine, fusing at 151° .

Erythrine.—Paul Juillard.—Natural erythrine, fusible at $146\text{--}148^{\circ}$, appears to the author to be a dianhydride derivative of anhydro-ortho-dicarboxic acid fixed to orcin and to picroerythrinic acid, $\text{C}_{10}\text{H}_{14}\text{O}_{20} + 2\text{H}_2\text{O}$. On treatment with HCl or CO_2 , anhydrodierythrinic acid is obtained; it is very soluble in acetone. The well-known erythrine so often examined during many years past, is found to consist of simple erythrine mixed with anhydrodierythrinic acid in variable proportions.

Method of Acylation in the presence of Pyridine.—P. Freundler.—At present the author is occupied with the question of benzoylation in the presence of pyridine, and in this paper he deals with the application of pyridine to the preparation of some amidised derivatives. It is generally admitted at the present time that pyridine and all the tertiary bases form molecular compounds with chloride of benzoyl, which are destroyed by water, with the formation of the chlorhydrate of the base and benzoic anhydride. This molecular compound is capable, not only of benzoylising, but it also acts as a dehydrant. The benzoylation takes place according to the equation $\text{XH} + \text{C}_6\text{H}_5\text{COCl} + \text{Pyr} = \text{Pyr.HCl} + \text{C}_6\text{H}_5\text{COX}$.

Method of Acylation in the presence of Pyridine. II. Application of Pyridine to the preparation of Amidised Derivatives, Symmetrical and Dissymmetrical.—P. Freundler.—A long paper, not suitable for abstraction.

Isomerism of Dibenzanilide.—P. Freundler.—The author concludes that there exists only one dibenzanilide, which crystallises in prisms fusible at $163\text{--}164^{\circ}$.

Chlorodinitrotoluene, $\text{C}_6\text{H}_2\text{CH}_2\text{ClNO}_2\text{NO}_2$ -1.3.4.6, and Chlorotrinitrotoluene, $\text{C}_6\text{H}_2\text{CH}_2\text{Cl(NO}_2)_3$ -1.3.2.4.6.—F. Reverdin, A. Dresel, and E. Delétré.—With the object of identifying more closely the product $\text{C}_6\text{H}_2\text{CH}_2\text{Cl(NO}_2)_2$ -1.3.4.6, already described, the authors have prepared several derivatives, which are here fully described. Among other bodies, they comprise oxydichlorophenyldinitrotolylamine, methoxyphenyldinitrotolylamine, and *p*-aminophenyldinitrotolylamine.

Chloronitrated and Nitrated Derivatives of 4-Oxy-2'.4'-dinitrodiphenylamine.—F. Reverdin and E. Delétré.—Not suitable for abstraction.

Some Diazoamidised Compounds.—Louis Meunier.—During his research on the formation of diazoamidised bodies, the author has prepared some derivatives not yet described. 10 grms. of nitro-orthotoluidine are dissolved in 200 c.c. of glacial acetic acid; add 2.3 grms. of nitrite of soda—that is, 1 molecule of nitrite for 2 molecules of amine. On the addition of water a yellow precipitate is formed, which, after crystallisation in acetone, takes the form of golden yellow crystals fusible at about 237° . Other bodies are also described and their constitutions given.

Diazoaminofuchsin and Diazoaminorosaniline.—L. Pelet and W. Redard.—By the close examination of the action of nitrous acid on fuchsin, the authors have observed that, besides the chloride of the diazoic, there is also formed a chloride of diazoaminofuchsin, by adding (in

the cold) a titrated solution of fuchsin in sufficient quantity to a solution of KNO_2 of known strength. It is necessary to operate in a slightly acid solution, in order to set free the nitrous acid. So long as the reaction is unfinished the solution has a yellow colour; the end of the reaction is indicated by the liquid becoming coloured red by the excess of fuchsin. Para-fuchsin and the new fuchsin (chlorhydrate of tri-para-amido-tritoly-carbhydride) behave in the same manner as fuchsin, and give the same corresponding derivatives.

Action of Sulphur on the Organo-magnesian Derivatives of the Dihalogenised Aromatic Hydrocarbides in the Nucleus.—F. Tarboury.—Already noticed.

Normal Glycerin in Blood.—Maurice Nicloux.—A controversial paper, not suitable for abstraction.

MISCELLANEOUS.

Messrs. Burgoyne, Burbidges, and Co., have just issued a New Edition of their Price List of Pure Chemicals, Reagents, &c.; it has been carefully revised and brought up to date. In Part II. will be found a complete list of chemical and physical apparatus. The whole is conveniently arranged, and should not be overlooked by users of chemical apparatus and materials.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 3rd inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President in the Chair. Mr. J. J. Duveen, Mrs. Green-Thompson, Mr. P. Hall, Dr. T. W. Hall, Dr. R. Liveing, Mr. J. M. McDonnell, Mr. C. Mitchell, Mr. J. H. Reeves, and Dr. J. J. H. Teall, F.R.S. were elected Members.

The London Essence Co.—The half-yearly report of this company has just reached us. It is pointed out that since the publication of the last report the recorded work on essential oils has not been very extensive, although a good many papers have been published dealing with the theoretical aspect of the constituents of essential oils. The successful synthesis of the terpene dipentene, by Dr. Perkin, is important, as it promises to help to settle the hitherto much disputed questions as to the constitution of the various terpenes. The first part of the report deals with essential oils, and the second part with recent researches. The report will be sent to any reader on receipt of a post-card.

The Chemical Laboratory at Wiesbaden.—During the Winter Term, 1904-05, there were thirty-eight students on the books. Of these twenty were from Germany, four from Russia, four from Spain, two from England, two from France, and one from Holland, Hungary, Egypt, Argentina, Chile, and Australia. There were three Assistants in the Instruction Laboratory, and 22 in the Versuchsstationen (private laboratories). To the teaching staff of the Institution belong the Directors, Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof. Dr. E. Hintz, and also Prof. Dr. Med. G. Frank, Dr. L. Grünhut, Dr. E. F. Grosse, and Architect J. Huber. The next Summer Term begins on April 25th. In the Winter Term, 1904-05, besides scientific work, there were many examinations carried on in the different departments of the Laboratory (Versuchsstationen) in the interest of trade, industry, mining, agriculture, hygiene, justice, and government.

Tantalum Filaments for Incandescent Lamps.—In the last report of the Committee of the "Société d'Encouragement pour l'Industrie Nationale" we find some interesting data concerning the new tantalum incandescent lamps recently placed on the market by Messrs. Siemens and Halske. Many years ago the use of platinum was abandoned in favour of carbon filaments. Quite recently,

however, Nernst introduced lamps having the filament formed of oxide of magnesium and the rare earths. Osmium has also been tried, but no definite opinion as to its real value can be given yet. Vanadium and niobium have also been used. The latest lamp is the one in which the filament is made of tantalum, a metal having an atomic weight four times as high as that of vanadium; this metal is obtained from the double fluoride of tantalum and potassium in the form of a powder, which is then fused *in vacuo*. The pure metal thus obtained resists the action of all alkalis and acids, with the exception of hydrofluoric acid; its density is 16.8, a very high figure; its resistance to traction is 95 kilos. per square m.m.; it is malleable, and can be drawn out into very fine wire. Its coefficient of dilatation is 0.000008 between 0° and 60°. The resistance of a wire of 1 sq. m.m. sectional area and 1 metre in length, between 0° and 100°, is 0.165 ohm. The filament of a 110 volt lamp must be very long, viz., 650 m.m., on account of its high conductivity; its diameter is only 0.05 m.m., and it gives the light of 25 Hefner candles, with a current energy of 1.5 volts per candle, or one-half less than lamps with a carbon filament. This long filament is coiled in a zigzag manner round the radial arms of two stars on metallic supports; the dimensions of the bulb are the ordinary ones. This filament is said to last as long as those of carbon, and offers a better resistance to accidental increases of voltage and to shocks and vibrations. Thus it is a filament full of promise for the future, and being brought out by a well-known firm, may be reasonably expected to stand the test of time.

MEETINGS FOR THE WEEK.

- TUESDAY, 12th.**—Royal Institution, 5. "Tibet," by Perceval Laodon.
WEDNESDAY, 12th.—Society of Arts, 8. "The Industrial Resources of the State of Matto Grosso, Brazil," by George Torrance Milne, F.R.G.S.
THURSDAY, 13th.—Royal Institution, 5. "Synthetic Chemistry" (Experimental), by Prof. R. Meldola, F.R.S.
FRIDAY, 14th.—Royal Institution, 9. "The Law of Pressure of Gases below Atmosphere," by The Right Hon. Lord Rayleigh, O.M., F.R.S., &c.
— Physical, 8. "On Ellipsoidal Lenses," by Mr. R. J. Sower, "Determination of the Moment of Inertia of the Magnets used in the Measurement of the Horizontal Component of the Earth's Field," and Exhibition of a series of Lecture Experiments illustrating the Properties of the Gaseous Ions produced by Radium and other Sources, by Dr. W. Watson.
SATURDAY, 15th.—Royal Institution, 3. "Some Controverted Questions of Optics," by The Rt. Hon. Lord Rayleigh, O.M., F.R.S., &c.

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DIRECTORS.

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Prof. W. FRESENIUS, Ph.D.
Prof. E. HINTZ, Ph.D.

LECTURES.

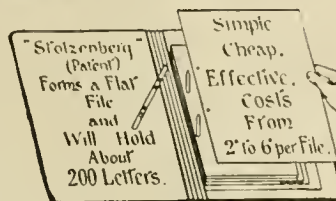
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Chemical Technology { Prof. H. FRESENIUS, Ph.D.
Prof. W. FRESENIUS, Ph.D.
and Prof. E. HINTZ, Ph.D.
Microscopy, with exercises in Microscopic work Prof. Dr. med. G. FRANK.
Chemistry and Analysis of Foods J. HUBER.
Hygiene
Practical exercises in Bacteriology
Technical Drawing, with exercises

The next Session commences on the 25th of APRIL. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KREIOL'S Verlag, at Wiesbaden, or to one of the Directors.

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THE CHEMICAL NEWS.

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STUDIES ON ENZYME ACTION.*

VI. THE SUCROCLASTIC ACTION OF ACIDS AS CONTRASTED WITH THAT OF ENZYMES (Part II.).

By EDWARD FRANKLAND ARMSTRONG, Ph.D.,
Salters' Company's Research Fellow,

and
ROBERT JOHN CALDWELL,
Clothworkers' Scholar, Chemical Department, City and Guilds of
London Institute, Central Technical College.

Hydrolysis of Cane-sugar by very Dilute Acids.

IN accordance with the theory put forward in our former paper (*Proc. Roy. Soc.*, lxxiii., 526), it was to be expected that on hydrolysing cane-sugar with sufficiently dilute acids the course of the change would not follow the simple logarithmic law, but that it would approximate, during the earlier period, to a linear function of the time. This supposition has been confirmed by experiments made very carefully to test this point.

Experimental Method.—In order that hydrolysis should be about half completed in ten hours by N/500 chlorhydric acid, it was necessary to work at about 40°. At this temperature, when so weak an acid is used, the solution does

not show any trace of colour even after four days, which may be regarded as evidence that no decomposition of the levulose into acid substances has occurred. In order to maintain the temperature at 40°, a stream of water was passed through the jacket of the polarimeter tube in which the hydrolysis was carried out. The water was taken from the mains at nearly 18° and passed through a metal vessel, about 2 litres in capacity, in which it was heated by a Bunsen burner to 30°. It was then passed through a metal vessel holding about 5 litres, containing an Ostwald thermoregulator; in this the temperature of the water was raised to about 39°. The final adjustment was performed by a very sensitive Ostwald thermoregulator with fluted sides to make it respond quickly to changes in temperature; this was placed in a cylindrical Dewar vacuum vessel, which it almost filled. After passing through a thin copper drum holding about 150 c.c., the water circulated through the regulator, cooling being prevented by the vacuum jacket; the temperature of the water in the drum was maintained at 40° by means of a flame controlled by the regulator. This arrangement proved to be eminently satisfactory in observing slow rates of change, although the extreme variation of the temperature was nearly $\pm 1/10$ th of a degree; the period of the variations was only one minute, so that in experiments extending over several hours the temperature variation was of no account.

The strength of the acid selected was N/500 hydrogen chloride; the two sugar solutions used contained 171 and 342 grms. sucrose per litre. The polarimeter tube had been in use for a considerable time with acid solutions. The solutions of sugar and acid were accurately measured out from burettes into a small flask into which steam had been passed, according to Ostwald's directions, to free it from alkali. The mixture was then rapidly filtered into the

* A Paper communicated to the Royal Society, August 26, 1904.

TABLE I.

Time in minutes.	α _D .	Average difference per thirty minutes.	K.
0	22°22	—	—
15	21°83	—	412
30	21°40	82	437
45	21°00	—	437
60	20°63	81	430
75	20°18	—	445
90	19°77	80	449
105	19°45	—	438
120	19°00	80	449
135	18°63	—	448
150	18°27	72	447
165	17°92	—	446
180	17°52	75	451
195	17°18	—	449
210	16°83	70	450
225	16°47	—	451
240	16°17	68	448
255	15°78	—	453
270	15°43	73	454
285	15°05	—	459
300	—	—	—
315	—	—	—
330	—	—	—
345	13°87	54	455
360	13°57	—	454
375	13°25	62	455
390	12°95	—	556
405	12°65	57	457
420	12°42	—	454
435	12°13	55	454
450	11°85	—	453
465	11°58	54	455
480	11°32	—	455
495	11°07	52	454
510	10°80	—	455
525	10°58	49	453
Complete change	—5°37	—	—

TABLE II.

α _D .	Average difference per thirty minutes.	K.
22°12	—	—
21°73	—	414
21°35	77	411
20°97	—	412
20°58	76	417
20°22	—	415
19°82	77	422
19°45	—	423
19°03	76	431
18°72	—	425
18°37	69	425
18°00	—	427
17°60	77	433
17°23	—	436
16°90	67	435
16°60	—	433
16°27	65	433
15°93	—	434
15°60	66	435
15°27	—	437
14°93	65	439
14°63	—	438
14°30	65	441
13°95	—	444
13°68	61	442
13°35	—	445
13°10	55	443
12°83	—	442
12°53	58	444
12°23	—	445
11°97	53	445
11°73	—	443
11°48	50	443
11°23	—	443
11°03	45	440
—	—	—
—5°37	—	—

TABLE III.

Average difference per
thirty minutes.

K

Time in minutes.	av.		K
0	46'03	—	—
10	45'47	—	428
20	44'83	—	461
30	44'20	—	471
40	43'62	185	468
50	42'97	—	478
60	42'37	—	479
70	41'80	182	477
80	41'17	—	482
90	40'57	—	485
100	40'07	175	488
110	39'45	—	483
120	38'85	—	486
130	38'28	176	487
140	37'67	—	491
150	37'13	—	490
160	36'55	173	492
170	36'03	—	491
180	35'43	—	495
190	34'93	167	494
200	34'45	—	492
210	33'87	—	495
220	33'38	156	494
230	32'87	—	494
240	32'38	—	494
250	—	152	—
260	31'28	—	499
270	30'80	—	499
280	30'38	154	496
290	29'87	—	498
300	29'48	—	495
310	28'83	144	502
320	28'42	—	500
330	27'93	—	501
340	27'43	146	503
350	26'97	—	503
360	26'55	—	503
370	26'12	134	503
380	25'65	—	504
390	25'25	—	504
400	24'87	126	502
410	24'42	—	503
420	24'02	—	503
430	23'62	124	503
440	23'17	—	504
450	22'80	—	503
460	22'38	123	504
470	21'93	—	506
480	21'53	—	507
490	21'13	123	507
500	20'77	—	507
510	20'40	—	507
520	20'00	112	508
530	19'68	—	506
540	19'27	—	508
Complete change	— 11'12	—	—

TABLE IV.

Average difference per
thirty minutes.

K.

av.		K.
44'63	—	—
44'02	—	481
43'37	—	489
42'75	—	493
42'20	183	487
41'58	—	492
40'93	—	500
40'30	186	505
—	—	—
39'10	—	507
38'47	183	512
37'87	—	513
37'28	—	515
36'70	178	516
36'13	—	516
35'53	—	519
34'95	177	521
34'33	—	525
33'78	—	526
33'25	168	525
32'73	—	525
32'25	—	523
31'65	158	527
31'13	—	527
30'65	—	526
30'13	154	527
29'62	—	528
29'08	—	530
28'60	152	530
28'15	—	529
27'63	—	530
27'22	142	528
26'72	—	530
26'28	—	529
25'83	138	529
25'32	—	532
24'88	—	532
24'47	135	531
24'02	—	532
23'60	—	531
23'15	130	532
22'73	—	532
22'35	—	531
Complete change	— 10'79	—

polarimeter tube. The first reading was taken ten or fifteen minutes after mixing, when the temperature had attained to that of the thermostat.

As, under these conditions, the rotatory power of the solution fell quickly, the polarimeter readings had to be taken very rapidly, so that the possible error in the tabulated values (although amounting to only 0.1 per cent) is about 0.03°, making a possible error of 3 units in the third column of differences.

By taking a very large number of points, such minor errors are eliminated, and when the velocity constant *K* is calculated according to the usual logarithmic law a very steady series of values is obtained.

From Tables I. to IV. it will at once be obvious that the value of the velocity coefficient *K* steadily increases during

about the first four or five hours of the change and then remains constant, the figures obtained being in striking contrast with those of Ostwald and also with those given later in this paper (Tables VI., VII.) for experiments in which stronger solutions of acid were used. In all these experiments the successive values of *K* vary up and down on either side of a mean value.

The fact that the value of *K* rises is an indication that change proceeds faster than the mass-action law requires. On the other hand, the figures do not offer definite evidence that the change proceeds at a strictly linear rate, although in all cases—especially that recorded in Table II.—the approximation to a straight line law during the first two and a-half hours is very close; indeed, if the possible error in the difference be taken into account, the first 10 or 15

TABLE V.—17.1 grms. Sucrose
per 100 c.c.

Time.	α_0 .	$\frac{10^4}{t} \log \frac{a}{a-x}$.
0	+21.55	—
15	20.40	[11.83]
30	19.30	[11.81]
45	18.27	11.70
60	17.33	11.50
75	16.40	11.44
90	15.43	11.56
105	14.60	11.45
120	13.75	11.46
135	12.95	11.44
150	12.10	11.55
165	11.37	11.51
180	10.65	11.51
195	9.93	11.54
210	9.30	11.49
225	8.62	11.54
240	8.02	11.52
Complete change	-7.18	—
Mean		11.52

TABLE VI.—17.1 grms. Sucrose
per 100 c.c.

α_0 .	$\frac{10^4}{t} \log \frac{a}{a-x}$.
+21.62	—
20.42	[12.32]
19.47	11.23
18.48	11.14
17.48	11.23
16.55	11.21
15.53	11.46
14.70	11.37
13.90	11.29
13.12	11.25
12.35	11.25
11.33	11.35
10.87	11.27
10.13	11.34
9.42	11.39
8.90	11.25
8.25	11.29
-7.18	—
Mean	11.29

TABLE VII.—17.1 grms. Sucrose
+ 9.0 grms. Glucose per
100 c.c.

α_0 .	$\frac{10^4}{t} \log \frac{a}{a-x}$.
+30.72	—
29.53	[10.93]
28.37	12.37
27.22	12.55
26.17	12.50
25.25	12.25
24.25	12.34
23.33	12.32
22.38	12.43
21.45	12.55
20.67	12.49
19.87	12.51
19.10	12.53
18.30	12.63
17.65	12.57
17.03	12.52
16.42	12.49
+2.03	—
Mean	12.47

TABLE VIII.—17.1 grms. Sucrose
+ 9.0 grms. Glucose per
100 c.c.

Time.	α_0 .	$\frac{10^4}{t} \log \frac{a}{a-x}$.
0	+30.63	—
15	29.45	12.20
30	28.25	12.58
45	27.13	12.60
60	26.15	12.33
75	25.12	12.39
90	24.12	12.46
105	23.15	12.54
120	22.23	12.58
135	21.33	12.65
150	20.45	12.74
165	19.67	12.72
180	19.00	12.59
195	18.18	12.73
210	17.48	12.73
225	16.80	12.75
240	16.13	12.80
Complete change	+2.03	—
Mean		12.59

TABLE IX.—17.1 grms. Sucrose
+ 9.0 grms. Fructose per
100 c.c.

α_0 .	$\frac{10^4}{t} \log \frac{a}{a-x}$.
+4.35	—
3.18	12.07
2.03	12.22
+0.95	12.19
-0.10	12.22
1.08	12.17
2.05	12.20
2.97	12.20
3.85	12.20
4.70	12.21
5.55	12.27
6.30	12.23
7.07	12.27
7.82	12.32
8.48	12.28
9.07	12.20
9.77	12.29
-24.30	—
Mean	12.22

TABLE X.—17.1 grms. Sucrose
+ 9.0 grms. Fructose per
100 c.c.

α_0 .	$\frac{10^4}{t} \log \frac{a}{a-x}$.
+4.24	—
3.13	12.59
1.97	12.55
+0.92	12.31
-0.10	12.22
1.10	12.22
2.13	12.37
3.05	12.26
3.90	12.29
4.82	12.41
5.65	12.43
6.43	12.43
7.20	12.45
7.93	12.47
8.63	12.48
9.25	12.43
9.93	12.49
-24.30	—
Mean	12.38

per cent of the change is practically linear. When the values are plotted on rectangular co-ordinates, the curve obtained falls between the straight line and the mass-action curve.

Furthermore, Tables III. and IV. indicate that the approximately linear portion of the change persists the longer the larger the proportion of sugar to acid.

It is obvious from these results that the analogy between acid and enzyme action is complete. In both cases, when the proportion of hydrolyst is relatively small the change is at first approximately a linear function of the time and subsequently a logarithmic function; whilst when a larger proportion of hydrolyst is present, the change is from the first a logarithmic function which may become modified by secondary causes. The association theory of hydrolysis put forward in these papers gives a very satisfactory explanation of the observed phenomena; as before stated, the differences between acid and enzyme action can all be attributed to the crystalloid nature of the former and the colloid nature of the latter.

Influence of the Products of Change.—In view of the

theoretical importance of the influence of the products of change (*loc. cit.*, p. 534), it appeared desirable to extend our experiments in this direction to cane-sugar. Accordingly the effect of adding 9 grms. of glucose or fructose to 100 c.c. of 17.1 per cent sucrose containing half a gram-molecule of hydrogen chloride has been determined in the manner previously described by one of us for β -camphor sulphonic acid at 20°. The results are incorporated in Tables V. to X.

Calculating from the equation $K = K_1[1 + 0.0131\rho]$, given by Arrhenius as that expressing the influence of concentration ρ on the constant of hydrolysis, it follows that, in the case of a solution containing 17.1+8.55 grms. of cane-sugar per 100 c.c., $K = 12.45$. The results obtained may thus be summarised—

TABLE XI.

	Mean value of K.
i. 9.0 grms. glucose	12.53
ii. 9.0 „ fructose	12.30
iii. 9.0 „ invert sugar (mean of i. and ii.)	12.42
iv. 8.55 „ cane-sugar (calc.)	12.45

It will be seen that about the same increase in the value of K is produced by equimolecular proportions of glucose and fructose, whilst the molecular effect of the biose cane-sugar is about twice the molecular effect of the monose.

The acceleration brought about by the addition of sugars may be attributed to a withdrawal of water by the sugar and the consequent increase in the amount of the "active system," as pointed out in our previous paper.

THE ELEMENTARY CHARACTER OF THORIUM.

By R. J. MEYER and A. GUMPERZ.

IN the *Journal of the American Chemical Society* (1904, xxvi., 922) Ch. Baskerville has published an article entitled "Thorium, Carolinium, Berzelium"; it forms the continuation of a former communication in the same journal (*Ibid.*, 1901, xxiii., 761). In these two articles the author endeavours to prove that the substance which we have known as thorium since its discovery by Berzelius is not elementary, but is a mixture of at least three elementary constituents. Although Baskerville's investigation is not yet concluded, in view of the great interest of the subject it may be worth while examining the other side of the question. We have resolved to undertake this investigation the more readily because Baskerville himself in his second article repeatedly invites others to assist in solving the problem.

According to Baskerville's observations thorium can be split up by two different methods, namely—(1) by fractional precipitation with phenyl hydrazine, and (2) by fractional sublimation of anhydrous thorium chloride. Setting aside the first method, which according to Baskerville presents many technical difficulties, and which was therefore abandoned by him, the chloride sublimation method gave the following result:—If pure thorium dioxide, mixed with sugar carbon, was heated in a quartz tube in a current of chlorine, by suitable regulation of the temperature and period of heating, the chloride formed could be decomposed into three fractions of different volatility. If the oxides were prepared from these, they exhibited very noteworthy physical and chemical differences after they had been subjected to various purifying operations. In particular—and this is the point which is to be specially examined here—the atomic weights of the metal in the three fractions differed very much from one another, as the following summary shows:—

1. Berzelium: Chloride most volatile; atomic weight, 212.
2. Thorium: Chloride of mean volatility; atomic weight, 220.
3. Carolinium: Chloride least volatile; atomic weight, 255.

Other differences appeared in the colour, specific gravity, and solubility of the oxides, as well as in the extent to which the chlorides may be hydrolysed, and in certain precipitation reactions with organic bases and acids. The degree of radio-activity also differed.

1. The Original Material.

Baskerville alludes only incidentally and indefinitely to the origin and degree of purity of the material used by him. He employed "pure thorium oxide from various sources," including a specimen prepared by Cleve for an atomic weight determination.

Commercial thorium nitrate as used in the incandescent light industry is nowadays a product of a very high degree of purity. The amount of foreign rare earths—cerium and yttrium earths—present in good preparations ought not to exceed some hundredths per cent on an average; lime, magnesia, alkali, and iron may be shown to be the chief impurities present in many products. Muthmann and Baur (*Ber.*, 1900, xxxiii., 2028) have shown how, by fractional precipitation with potassium chromate, an

absolutely pure thorium can be prepared from the commercial product. By the method described by these authors we have decomposed about 700 grms. of thorium nitrate into seven chromate fractions. The chromates were decomposed by boiling with pure caustic potash in platinum dishes, and the hydroxides thus obtained were carefully washed, dissolved in hydrochloric acid, and precipitated with oxalic acid. The oxalates were finally taken up in a concentrated solution of ammonium oxalate, and again separated by means of concentrated nitric acid. As it was conceivable that on fractionating with potassium chromate a partial splitting up of the thorium might have occurred, especially as this method when applied to the separation of the cerium and yttrium earths had proved itself to be exceptionally effective, according to the observations of Muthmann and his pupils, equivalent weight determinations were performed, using the thorium oxides prepared from Fractions I., IV., and VII.

2. Determination of the Equivalent Weight of Thorium.

Baskerville determined the equivalent weight of his thorium fractions by the conversion of a weighed quantity of the oxide into anhydrous sulphate. It is to be regretted that he did not describe more fully the method he adopted. A more detailed account of his work would be all the more desirable, because the method he chose has never yet been used for the determination of the atomic weight of thorium; and with good reason, for while this method is known to give good results when applied to the elements of the cerium and yttrium earths,* even if some uncertainty attaches to it, we are *a priori* inclined to regard it doubtfully when the equivalent weight of thorium is to be determined, for it is obvious that, in view of the feebly positive character of this element, the point of actual neutrality of the sulphate on evaporation of the oxide with sulphuric acid will be much more difficult to determine than in the case of the more strongly basic oxides of the other rare earths. This doubtfulness regarding the method would be increased by the consideration that small errors in the method would be of all the greater importance because of the high atomic weight.

As a matter of fact, if the sulphate method is employed the equivalent of thorium is determined by the reverse process, namely, the conversion of the sulphate into the oxide. From what has just been said it follows that the sulphate anhydride prepared directly from the oxide must not be employed, but a crystallised hydrate which by cautious dehydration may easily be converted into neutral anhydride.

Krüss and Nilson (*Ber.*, 1887, xx., 1665), to whom we owe the first really satisfactory determination of the atomic weight of thorium, used this method. These authors especially emphasise the fact that their attempts to obtain a product of constant composition from the oxide by treatment with sulphuric acid were always unsuccessful. Our experience is exactly the same. Although, after driving off most of the excess of sulphuric acid, we varied the temperature within wide limits, and repeated the operation several times, we could never get uniform results, although the weight at a given temperature became constant. The attempts to determine the equivalent by this method gave values which varied within the widest limits.† If Baskerville has succeeded with this method a discussion of his determinations must be deferred until detailed information concerning the conditions observed by him are given, and particularly until it has been proved that the sulphate he weighed had the normal composition;‡

The method which proved successful in our hands consisted in the dehydration of thorium sulphate octohydrate

* With the exception of cerium, when this method fails for the same reason as in the case of thorium.

† It might here be a case of equilibria between acid, neutral and basic sulphate, varying with the temperature.

‡ Baskerville's weighings are given to six places of decimals, and the equivalents calculated from them to three places, which testifies to an exaggerated confidence in the method.

at 400°, and the conversion of the weighed anhydride into dioxide by ignition before the blowpipe, *i.e.*, in the determination of the proportion $\text{Th}(\text{SO}_4)_2:\text{ThO}_2$. For this purpose the fractions to be tested were converted into oxide, and a portion finely powdered was moistened with water in a platinum dish, and repeatedly evaporated with concentrated sulphuric acid, without being raised to a red heat. The powdery dry sulphate thus obtained, which, however, was not completely free from acid salt, was finely powdered and introduced into ice water, being meanwhile automatically stirred; if any insoluble residue remained it was again treated with sulphuric acid. The solution was then evaporated to crystallisation at 30–35°, so that almost all the dissolved salt crystallised out as octohydrate.* After the crystals had been dried in the air or kept for a short time in the desiccator, about 2 grms. were weighed out into a platinum crucible, which was then gradually heated to 400° in a small electric furnace; this temperature was maintained until the weight became constant. The temperature was measured by means of a thermo-element with a millivoltmeter graduated to degrees of temperature. The anhydride thus obtained was cooled over phosphorus pentoxide, and the crucible then weighed as quickly as possible in a previously tared closed weighing tube. By strongly heating for a long time before the blowpipe, the sulphate was finally converted into oxide; the weighing must be performed with the same precautions as before. But W. Biltz (*Ann. d. Chem.*, 1904, cccxxxi., 356 ff.) has recently called attention to the fact that even if all moisture is absolutely excluded it is very difficult to get the weight of ignited thorium oxide perfectly constant; however, the oxide obtained from the sulphate shows the property of absorbing gases on ignition to a much less degree than the oxide obtained by Biltz from the acetyl acetate, as it is less finely divided.

This source of error has thus only a slight influence on our determinations, and could be neglected by us, especially as in our experiments it was not a question of atomic weight determinations in the strict sense of the word. Moreover, it may easily be calculated that when 1 gm. of $\text{Th}(\text{SO}_4)_2$ is used an error of 1 m.grm. in weighing the oxide alters the value of the atomic weight by 0.7 unit. The method described is, according to our experience, the only trustworthy one for obtaining a neutral sulphate anhydride. It is specially important that the feeble acid solution of the sulphate should not be evaporated at a temperature exceeding 40°, so that the tetrahydrate can separate out.† The latter, if it crystallises from acid solution, contains some free sulphuric acid, which does not completely pass off on heating to 400°. Under such conditions, therefore, the values of the equivalent weight obtained are too low. This source of error is specially marked if the sulphate solution is evaporated at about 70°, when pure tetrahydrate separates out.

The equivalent was determined by the method described above, using chromate Fractions I., IV., and VII. The results are collected in the following table:—

Fraction.	Hydrate used in grm.	Anhydride weighed in grm.	H ₂ O per cent.	ThO ₂ weighed in grm.	Atomic weight.
I.	1.2463	0.9301	25.37	0.5793	232.4
I.	1.3261	0.9927	25.14	0.6184	232.5
IV.	1.3910	1.0344	25.63	0.6442	232.3
IV.	1.2543	0.9349	25.46	0.5821	232.2
VII.	0.8934	0.6680	25.23	0.4160	232.3
VII.	—	0.4296	—	0.2676	232.5

* The water determinations given below show that possibly under these conditions some hydrates containing 9 molecules of water crystallised out, as well as the octohydrate. This agrees with Roozbeom's observations (*Zeit. für Phys. Chem.*, 1890, v., 198). The relative stability of the two hydrates has not yet been accurately determined.

† The conversion of octo- and eonea-hydrate into tetrahydrate occurs according to Roozbeom (*Zet. für Phys. Chem.*, 1890, v., 198) at 43°, and according to Dawson and Williams (*Proc. Chem. Soc.*, 1899, xv., 211) at 47°.

The most accurate value of the atomic weight of thorium is now taken as 232.5. Thus the determinations given above show that the decomposition of the original material into the seven chromate fractions does not show any indication of the possibility of splitting up thorium.

3. Sublimation of Thorium Chloride in a Current of Chlorine.

We now used the method adopted by Baskerville. This depends upon the decomposition of anhydrous thorium chloride into three portions of different volatility. It appeared to us not desirable to follow Baskerville's method exactly for this purpose, *i.e.*, to prepare the chloride by Berzelius's old and inconvenient method of igniting the oxide mixed with carbon in a current of chlorine. We preferred to employ a process recently described by Matignon (*Comptes Rendus*, 1904, cxxxviii., 631), and tested by us, *i.e.*, heating the oxide in a mixture of chlorine gas and vapours of sulphur monochloride. We give here a short description of the method we finally adopted after several preliminary experiments.

A porcelain boat filled with thorium oxide was heated in a long porcelain tube in a large electric resistance furnace. This furnace, when the current intensity obtainable was 35 to 40 amperes, gave a maximum temperature of 1300°. The chlorine gas drawn from a bomb passed first through some wash-bottles containing sulphuric acid, and then entered a double tubulated spherical vessel filled with sulphuric acid, which was heated by a small luminous flame, and then passed into the tube charged with sulphur monochloride vapour. This tube projected into a second vessel, which was intended for the collection of the most volatile sublimate.

With this arrangement we observed exactly the same phenomena as those described by Baskerville in his article. At about 800° white clouds began to sublime into the vessel, which was cooled with ice, and to condense on its walls as a fine yellow deposit (I.). A part of this light sublimate was carried by the current of gas into the tubes serving to lead away the chlorine. On raising the temperature this part increased, although the quantity of sublimate going over seemed to decrease on long continued heating. The temperature was then kept for a further period (1 to 3 hours) at 1200°. The walls of the tube were then covered with beautifully crystallised chloride (II.), and the contents of the little boat were also completely converted into chloride (III.) after the heating had been continued long enough. In general 5 to 10 grms. of thorium oxide were used; with smaller quantities often the whole contents of the little boat were volatilised. The residue remaining in the little boat (III.) was repeatedly converted into oxide in many experiments, and this oxide again subjected to sublimation; the phenomena, however, in these repetitions were qualitatively and quantitatively the same as in the first sublimation. As material for these experiments sometimes oxides of the chromate fractionation were used, and sometimes an oxide which was prepared directly from commercial thorium nitrate, and which was thus not purified. Baskerville has subjected his three chloride fractions to different and very energetic purification processes in order to free them from adulterations arising from the carbon and the quartz tube. As in the method we adopted the only impurities that could be present were traces of sulphur, aluminium, silicic acid, and alkali, we thought that we should be able to dispense with such treatment all the more readily because the above method used by us for the equivalent weight determination *per se* formed a very effective purification process, and undoubtedly guaranteed the removal of the above impurities.

FRACTION I. *Contents of the Vessel (Berzelium).*—The contents of the vessel dissolved to a clear solution in water. The solution was precipitated with oxalic acid, after addition of hydrochloric acid, and the oxalate ignited to oxide. The determination of the atomic weight gave:—

Hydrate used.	Anhydride weighed.	H ₂ O per cent.	ThO ₂ weighed.	Atomic weight.
Grm.	Grm.		Grm.	
1.2573	0.9199	26.84	0.5730	232.5
1.0424	0.7647	26.65	0.4764	232.6

According to this, in the most volatile portion in which Baskerville found the atomic weight to be 212, the atomic weight is quite unchanged. We cannot say how this contradiction is to be explained. But we have no doubt that we have obtained the same product as Baskerville. As regards the nature of the "weisser Dampf" which Berzelius has already observed, and which passes over especially at the beginning of the sublimation, it appears that it contains much oxychloride; we reserve for the present the analytical proof of this.

FRACTION II. *Product of Mean Volatility (New Thorium).*—The beautifully crystallised chloride which was deposited on the walls of the tube gave the following results in atomic weight determinations:—

Hydrate used.	Anhydride weighed.	H ₂ O per cent.	ThO ₂ weighed.	Atomic weight.
Grm.	Grm.		Grm.	
—	1.0650	—	0.6635	232.4
1.0387	0.7758	25.31	0.4834	232.7

This part also, which, according to Baskerville, contains the new thorium, freed from berzelium and carolinium, and having the atomic weight 220, showed no alteration in our atomic weight determinations.

FRACTION III. *Contents of the Little Boat (Carolinium).*—The information which Baskerville gives concerning the properties of the sublimate residue is specially noteworthy. The atomic weight in this fraction rises to 255. The oxide, moreover, which possesses a greyish-red colour, is said to be soluble in concentrated hydrochloric acid, while the oxides of "berzelium" and of the "new thorium" do not possess this property. The reddish colouration of a thorium dioxide has hitherto generally been taken to show the presence of certain impurities. Apart from this a modification of ordinary thorium dioxide is known, the so-called thorium meta-oxide, which has the same properties as the ordinary oxide, but is specially distinguished by its reddish colour, and on treatment with acids passes into soluble compounds the nature of which is still disputed. Baskerville's "carolinium oxide" vividly recalls in its properties the meta-oxide, yet he expressly emphasises the fact that it is not identical with this, without, however, giving further reasons for this assertion. Our residue, after repeated sublimation in a current of chlorine, also gave, as the two following determinations show, the normal atomic weight for thorium:—

Hydrate used.	Anhydride weighed.	H ₂ O per cent.	ThO ₂ weighed.	Atomic weight.
Grm.	Grm.		Grm.	
1.1904	0.8824	25.87	0.5496	232.4
0.7487	0.5545	25.91	0.3454	232.4

Thus our results completely contradict Baskerville's statements. The somewhat different experimental procedure which we adopted cannot be responsible for this, for the external phenomena, which were observed during the sublimation, were exactly the same as those described by Baskerville. The cause of this lack of agreement cannot be discovered till Baskerville has published detailed statements concerning his material and method. We do not, therefore, for the present enter upon a discussion of the other distinctions which he specified as existing between the three oxides he isolated. Only one point must be briefly touched upon. A fundamental criterion of the elementary nature of a substance is the individual selective light emission of its glowing vapour. Consequently, the three components separated by Baskerville from thorium, if they contain three atomically different substances, must undoubtedly exhibit differences in their spectra, even if they are not present in a perfectly pure state. Crookes

could discover no such differences when he submitted Baskerville's chloride fractions to a spectrographic examination. As this question is of special importance for the whole problem of the possibility of splitting up thorium, Dr. G. Eberhard, of the Royal Astrophysical Observatory in Potsdam, has undertaken to establish spectrographically both the arc spectra of the fractions obtained by us, and also of thorium preparations from other sources, with the help of the excellent apparatus of this Institute, and also to examine them minutely for differences. Dr. Eberhard will himself report upon the negative result of this investigation.*

Finally, we must expressly call attention to the fact that the above examination cannot decide the question of the elementary or compound nature of thorium. But according to the results so far obtained in the separation of the rare earths, we believe that the methods which will be best suited to solve the problem definitely are such as permit of differentiating the original material, if it is decomposable, according to the solubility or basicity of its constituents. Brauner (*Proc. Chem. Soc.*, 1901, xvii., 67) has already described the latter way some years ago, when he subjected thorium ammonium oxalate, $\text{Th}(\text{C}_2\text{O}_4\cdot\text{NH}_4)_4 + 7\text{H}_2\text{O}$, to fractional hydrolytic decomposition. The results thus obtained argue in favour of the possibility of decomposing thorium, but unfortunately Brauner's preliminary communication, which only comprised about a page, has not been followed by any further communication.—*Berichte*, 1905, xxxviii., 817.

A NEW IODISED COMPOUND OF OSMIUM, THE PRODUCTION OF WHICH GIVES A MEANS OF ESTIMATING VERY MINUTE QUANTITIES (MILLIONTHS OF A GRM.) OF OSMIUM IN SOLUBLE COMPOUNDS.

By Dr. EUGENIO PINERUA ALVAREZ,
Professor of General Chemistry of the Faculty of Sciences, Madrid.

OSMIUM has been studied by a large number of chemists, among whom, in the first place, we must mention Smithson Tennant, who discovered it in 1804, and immediately after him in chronological order come Vauquelin (1814), Dulong (1823), Berzelius (1820), Doebereiner (1835), Wöhler (1853), Deville and Debray (1859).

An important modification in the methods employed to extract the metal during the first half of last century is due to Deville and Debray in 1876.

Claus and Jacobi, from 1846 to 1863, published a series of remarkable experimental researches, which confirmed certain results and rectified others, amongst some of the most interesting being Berzelius's investigations on the compounds of osmium in general.

Fritzsche and Struve published, in 1846, their experiments on osmiamic acid and its salts, which were continued in 1892 by Joly, after important researches had been carried out with these substances by Dufet and Nordenskiöld.

We owe the study of the osmium cyanide compounds to Martius in 1860.

Wolcott Gibbs published his researches on osmium-ammonium combinations between 1858 and 1881.

Huggins (1864), Thälén (1868), and Gouy from 1879 to 1880, made numerous spectroscopic experiments with this metal.

Morah and Wischin, in 1893, published their works of revision, which, to the present day, are looked upon as the most important facts regarding osmium and its compounds; those referring to its combinations with the halogens are the most remarkable.

Lastly, amongst the chemists who have also contributed to the already very complete knowledge of osmium we must mention:—Mallet, Buttlers, Brinzard, Eichler, Behrens, Lecoq de Boisbandran, Meyer, and Seubert.

* Dr. Eberhard's paper will appear in our next issue.

We must not forget Max Schultz Ranvier, and especially Ot. Sule, Heraeus Mercier, Gibson, and Moul, who, in the closing years of last century (1893 to 1900), published some very interesting Applications of the Compounds of Osmium.

In repeating during the actual academical course—solely for the purpose of teaching—for the Chair of Analytical Chemistry of the Doctorship of Science—the important reactions proposed for the research, the separation and estimation of osmium, and wishing to determine accurately what are the best or most favourable circumstances for obtaining by the action of the proper reagents the successive products of the gradual reduction of the peroxide or tetroxide of osmium, OsO_4 (commercial osmic acid), in aqueous solution, I have succeeded in obtaining a new osmium hydriodide compound with the formula $\text{I}_2\text{Os}_2\text{IH}$, which has, when dissolved, a beautiful emerald green colour.

This compound has no great affinity for oxygen, and is as unstable as the corresponding ferrous compound, I_2Fe ; but it acquires great stability when giving rise to *iodo-osmities*, especially in the presence of concentrated, or, better, saturated, saline solutions, as, for example, those of potassium chloride, calcium chloride, &c.

The new green iodised compound of osmium is soluble in water, much more so in anhydrous sulphuric ether, and is insoluble in benzoic acid and in chloroform.

On reacting with oxidising acids, as, for example, nitric acid, the solution immediately loses its green colour, and acquires the same red colouration which it presents after a certain time when left exposed to the action of the air.

Nitrites acting upon its acid solutions give rise to a black precipitate of hydrated dioxide of osmium.

It decolorises a solution of potassium permanganate, and reduces that of the chromate acidified with sulphuric acid.

The reaction which produces the new compounds is very easy of execution, absolutely characteristic, and of such extraordinary sensitiveness that it may be used for the colorimetric estimation of osmium in quantities of a millionth of a gramme. In the first experiments the reacting substances were pure concentrated hydrochloric acid of 22°Be , equally pure potassium iodide, and the aqueous solution of the osmic compound (OsO_4).

I then substituted, with positive advantage, phosphoric acid of density 1.7 for the hydrochloric acid.

In fact, considering the importance of the peroxide or tetroxide of osmium in micrographic research, the compound is found very pure in commerce in all countries; so much so, that I have used it with great advantage in my research.

The quantities of the reacting substances were as follows:—

Aqueous solution of 1% iodide of potassium	2 c.c.
Pure concentrated hydrochloric acid of 22°Be or phosphoric acid of density of 1.7	20 drops
Aqueous solution of peroxide of osmium (commercial osmic acid) 1%, 1%, and 1%	1 drop

The method of working consists in pouring, by means of a pipette, the 2 c.c. of the solution of potassium iodide into a test-tube, immediately adding the 20 drops of hydrochloric acid, or better still, the phosphoric acid, shaking the mixture, and adding at once in the cold to the acidified solution of the iodide—which is colourless—one single drop (1/20 c.c.) of the aqueous solution of the osmium peroxide, and, after one or two minutes—shaking the liquid—the emerald green colouration of the osmium compound appears.

The reaction takes place between 1 molecule of OsO_4 and 10 of IH , $\text{OsO}_4 + 10\text{IH} = \text{I}_2\text{Os}_2\text{IH} + 4\text{H}_2\text{O} + 3\text{I}_2$.

In working with very dilute solutions of commercial osmic acid, it is well to add a small quantity of anhydrous sulphuric ether to the quantity of iodide acidified with hydrochloric or phosphoric acid, in order that the green iodide of osmium may dissolve in the supernatant layer of floating ether; the reaction is more sensitive on account of the diminution of the volume of liquid which contains this product.

If the solution of peroxide of osmium (OsO_4) was the commercial acid usually employed in micrographical laboratories, 1%, one single drop (1/20 c.c.) would be sufficient to produce an intense green colouration in the whole mass of liquid. If we add ether—which is not necessary in this case—it would dissolve out the iodised compound, colouring it green, and the rest of the liquid would appear colourless.

If we add pure benzene this liquid would acquire a gooseberry-red colour by dissolving out the free iodine produced in the reaction, and on shaking the mixture to favour the oxidation by the air of the green compound of osmium, the red colour of the benzene would increase in proportion as the iodine which would be liberated during oxidation was dissolved.

By using an osmic solution containing 0.0005 gm. of OsO_4 per c.c., one single drop (1/20 c.c.) containing 0.0000205 gm. of the compound of osmium, is sufficient to produce immediately the emerald green colours in the supernatant ether, which in this case it is convenient to use.

If we add anhydrous ether to the solution of potassium iodide, acidified with phosphoric acid, and then one or two drops of the 1% (1 in 10,000) aqueous solution, which contains five-millionths of a gm. (0.000005) of peroxide, a greenish tint is again seen in the ether layer.

It therefore follows that the production of this green compound of osmium can be used to detect the presence of thirty-seven ten-millionths of metallic osmium.

I have obtained the same reaction in decolorising by means of a fresh solution of sulphurous acid gas in water four or five drops of an aqueous saturated solution of potassium iodide and iodine, with which the osmic compound and ether had been previously mixed; this latter an excellent method for producing very stable green osmium iodide. The substances present in this case are sulphuric acid, great excess of potassium iodide, nascent hydriodic acid, and peroxide of osmium.

In some recent experiments I have substituted for the aqueous solution of iodine and potassium iodide, iodised hydriodic acid (hydriodic acid acted upon by light), and in adding the sulphurous acid solution, the osmium compound (OsO_4) being present, I obtained the green tint.

In this reaction free and nascent hydriodic acid, sulphuric acid, and the osmium compound (OsO_4) were present.

I made a new series of experiments, using only iodine, sulphurous acid gas, and the compound of osmium.

The best method of action in using these bodies is as follows:—

To 1 c.c. of diluted etherised solution of iodine, a single drop containing 1% of osmic anhydride (OsO_4) is added; the mixture is shaken, and then a slight excess of dissolved sulphurous acid gas is added, when immediately the ether layer appears tinted green. In all these experiments the liquid mass had a strong sulphurous odour.

The bodies reacting are sulphuric acid, nascent hydriodic acid, and the compound of osmium.

Finally, I used the diluted hydriodic solution, obtained by means of reacting in presence of water with iodine and sulphuretted hydrogen gas, eliminating the excess of the latter by heat, and the results were identical or almost identical. But we must point out that when using free hydriodic acid as a reagent, it must be used in great excess, and all at once, in order to produce osmium hydriodide of an emerald green colour without other intermediate yellow, grey, red, or black bodies.

The generating mixtures of hydriodic acid (nascent acid) which have been mentioned are much more to be recommended, for the same reason mentioned in connection with free hydriodic acid, more concentrated solutions of potassium iodide than the first which I used for the experiment quoted. And in order to obtain the stability of the green osmium compound, it is necessary to add salts, as, for example, that of potassium chloride, or better still, crystallised calcium chloride. After obtaining the free osmium solution, it is equally good to add to it several fragments

of pure calcium carbonate (Iceland spar) in order to neutralise the excess of phosphoric acid.

The excess of potassium iodide is excellent for the production of its corresponding iodo-osmite ($\text{I}_2\text{Os}, 2\text{IK}$). The elimination—by means of a few crystals of calcium carbonate (Iceland spar)—of the excess of phosphorus acid is necessary in order that the latter may not affect the osmic iodosal formed. The favourable influence in this case of the concentrated salt solutions can be explained very satisfactorily according to the well known theory of ionisation.

Making a choice among the number of experiments made which form the basis of the foregoing rules, we publish three of those which have produced a beautiful emerald green coloured stable liquid, which is purified by submitting it to the action of benzine (C_6H_6), in order to dissolve all the iodine set free during the reaction.

A.	1. Solution of potassium iodide (IK) 2 %	2 c.c.
	2. Medicinal phosphoric acid (PO_4H_3)	60 drops
	3. Osmic solution (OsO_4) 1 %	1 drop
	4. Saturated solution of crystallised calcium chloride ($\text{Cl}_2\text{Ca}, 6\text{H}_2\text{O}$)	2 c.c.
B.	1. Solution of potassium iodide (IK) 20 %	2 "
	2. Phosphoric acid (PO_4H_3)	1 "
	3. Osmic solution (OsO_4) 1 %	2 "
	4. Saturated solution of crystallised calcium chloride ($\text{Cl}_2\text{Ca}, 6\text{H}_2\text{O}$)	2 "
C.	1. Solution of potassium iodide (IK) 20 %	2 "
	2. Phosphoric acid (PO_4H_3)	2 "
	3. Osmic solution (OsO_4) 1 %	1 "
	4. Saturated solution of crystallised calcium chloride ($\text{Cl}_2\text{Ca}, 6\text{H}_2\text{O}$)	3 "

Instead of adding the saturated solution of calcium chloride to the solutions of osmium iodide, it is better to add the chloride in its solid state until saturation takes place, then the little crystals of Iceland spar may be added.

On washing the product with benzine it becomes a very pure green colour.

In conclusion, it follows from the preceding investigations that not only is hydriodic acid a good qualitative and quantitative reagent for osmium compounds, but also that the latter, especially the peroxide, are in their turn equally so for the iodides when in presence of chlorides and bromides.

THE IMPORTANCE OF ACCURATE MEASUREMENTS AT VERY LOW TEMPERATURES.*

By Dr. H. KAMERLINGH ONNES.

(Continued from p. 157).

THE law of corresponding states (for these researches placed by Dewar on a line with the second law of thermodynamics) revealed to us the importance of the knowledge of the equation of state of the same substance over the greatest possible range of reduced temperatures. It proves to us that the deviations of the different reduced models are no less important.

Of most substances, even of one investigated so exhaustively as carbon dioxide, hardly anything is known below zero. The investigation of the equation of state of water alone, according to Amagat, is sufficient to engross ten years of the life of a clever industrious physicist. He said this with a view to ordinary temperatures only. What an amount of work will be required to determine the deviations from the law of corresponding states over the whole range of reduced temperature!

This work once accomplished, however, it will be the equations of state which come to the front instead of the

quantities to be derived from them, which quantities are now still treated and determined rather as independent quantities, e.g., coefficients of compressibility, coefficients of expansion, coefficients of pressure variation, heat of evaporation, vapour tension, density of vapour and liquid which are in contact, differences between all sorts of specific heat and that in the rarefied gaseous condition. Then we shall know for each substance the general law of all those quantities which now are known generally only over a limited range. We shall have laid down the equation of state of each substance in one single image which will cover all these quantities—an empirical formula with twenty-five constants has been tried as such (*cf. Communications from the Physical Laboratory at the University of Leiden*, No. 74)—and it will be this empirical equation of state which will be looked up in tables, as we now, for instance, look up the empirical formula of a coefficient of expansion. Better still would be the complete surface of Gibbs, a model that embraces even more results of observations, a description of which, however, would lead us too far (*cf. Communications, &c.*, Nos. 66, 86).

When all these equations of state of the various substances, including the abnormal ones, are before us, combined into images, will the correspondence between these groups of models, with their striking deviations, still be as great a mystery to us as at present, or shall we have succeeded in explaining their correspondence and their deviations by the greater or less similarity in the chemical nature of the substances? We trust that the latter will be the case. It is certain that we must know the natural phenomena, and survey them as much as possible before we can explain them. To get to know the equations of state of the best known substances with sufficient accuracy down to the lowest temperatures seems indeed a task which will take up the greater part of the forces of experimental physics during the whole of the Twentieth Century.

In this sketch of the meaning and extent of the work which is waiting for us in this line only, I was guided by the law of corresponding states. Also our method of procedure is pointed out by this law.

As the law of corresponding states gives us already an approximate forecast of the behaviour of the normal substances, only accurate measurements can claim scientific value. Approximate determinations, which can at best decide whether a substance belongs to the normal ones or not, do not bring us any further.

Rapid progress in this field cannot therefore be expected, especially if we consider how few accurate results concerning the equation of state are obtained at the temperatures which have long been used in experimentation.

After Regnault and Andrews, Amagat and Young have become the leaders in this field. But how few only have succeeded in equalling these masters and obtaining valuable results! For some of the recent problems a higher degree of accuracy in measurements is required than in those of these great men. The determinations must be made according to a still higher degree of precision to test the law of corresponding states in the moderately condensed gaseous state (*cf. Communications, &c.*, Nos. 50, 67, 70) at which we can derive critical values from the deviations from Boyle's law (*cf. Communications, &c.*, Nos. 88 and 71), but at which the fourth powers of the densities may be neglected. To mention one point, it will be necessary to compare the pressure with a mercury column, a comparison rendered possible (*cf. Communications, &c.*, No. 44), because we need not, like Regnault, climb a tower, but are able to apply as high a pressure as he did by means of several small mercury columns arranged in parallel in an ordinary room, which together form the required height, while the pressure is transferred from the one to the other by compressed gas. For problems of the same kind work of this higher degree of accuracy will also be wanted at low temperatures, and we always need at least the accuracy reached by Young and Amagat at ordinary temperatures.

There are several reasons why this is difficult.

* Address delivered in commemoration of the 320th Anniversary of the University of Leiden. From *Communications from the Physical Laboratory at the University of Leiden*, Suppt. No. 9 to No. 85—96.

In the first place we lack at low temperatures a liquid like mercury, which renders such important services in all measurements at ordinary temperatures. Moreover, at low temperatures (for the measurements *cf. Communications, &c.*, Nos. 27, 60, 77, 85, 89) we lack the most fundamental determinations like those of which the results are at our disposal at ordinary temperatures. Thus the thermal expansion of glass has been determined only quite lately, and yet not even with the greatest accuracy (*cf. Communications*, No. 85). The corrections of the gas thermometer to the absolute scale are still entirely wanting. The great difficulty of the measurements lies especially in the circumstance that at a low temperature each degree gains so much more importance, while at the same time it becomes more difficult to keep the temperature constant, a thing of first moment in the measurements. In the case of hydrogen the temperature must be kept constant ten times more carefully than in researches at ordinary temperature. Even then to keep the temperature constant within the required limit of one-tenth degree is one of the greatest difficulties. With liquid hydrogen we must go to 1/100 degree.

If also we consider the uncertainty which still exists about the boiling-point of hydrogen, it is obvious that for accurate measurements at low temperatures, more is required than the mere preparation and decantation of the liquid gases which help to produce these temperatures.

(To be continued).

NOTICES OF BOOKS.

A Scheme for the Promotion of Scientific Research. By WALTER B. PRIEST. London: Stevens and Sons, Ltd. 1905.

WHILE the aim of this scheme is entirely laudable and merits the most whole-hearted support, the difficulties attendant on its working out and application seem almost insuperable. It is obviously very much easier to criticise a scheme of this kind when formulated than to draw up a better, and possibly the adoption of this or some similar plan might lead to the desired results, though it is hardly possible to be other than sceptical on this point. The author shows that, inasmuch as the inventor, by means of the Patent Laws, is enabled to obtain the pecuniary advantage which the successful working of his invention brings with it, the discoverer of new facts, which may be of the utmost importance, and yet have no marketable value, should have a claim to some similar monetary recompense. But in spite of its excellence of aim there are many weak points in the scheme; for instance, who can tell what results of general utility may come from a research in any particular direction? Of the hosts of new organic compounds which are being isolated almost daily, who shall say which may acquire some technical importance, and which will remain for ever of scientific interest only? Moreover, and this is a point of wider significance, it would be a Herculean task sometimes to accredit the right person with the merit of the discovery; for instance, taking the case of the isolation of a new chemical individual, one investigator discovers some general principle which may be applied to the preparation of new substances, such as the use of very low temperatures; hosts of workers set themselves to modify and improve the details of manipulation, &c., and of all the new substances prepared, one, which is isolated by a worker who may even possess no originality, but may simply apply another man's method to different reagents, may acquire great technical importance; which of these workers is to get the grant, or in the case of subdivision, how is it to be divided among them? It is quite conceivable that the actual preparer of this new substance would be the very one who was really least responsible for its preparation, and to trace back the actual merit through

the work of all the investigators would be practically an impossibility. Even supposing the discoverer, like the inventor under the Patent Laws, could claim a principle, the difficulty again recurs of how the importance of a principle is to be estimated until it has been repeatedly applied. It seems to us far more probable that the endowment of research would furnish the desired incentives, and it is surely casting a very singular slur on scientific workers to say that those who were paid to do research work would not, as a rule, do it successfully, and that the remuneration of such persons would lead to abuses in the application of the funds.

"N" Rays. By R. BLONDLÖT. Translated by J. GARCIN. London, New York, and Bombay: Longmans, Green, and Co. 1905.

THIS volume contains the translation into English of all Prof. Blondlot's papers on the subject of the "N" rays, communicated to the Academy of Sciences. The author describes in very simple and clear language the experiments he performed during his investigation of these rays, but the papers have probably been already read carefully by those who are interested in the study of radiation phenomena, and thus it hardly seems worth while to reproduce them in book form, especially at this stage of the investigation, when the rays have not been thoroughly studied nor even their existence accepted as proved. The last paper included is dated March, 1904. The book contains some illustrations and notes on making phosphorescent screens, as well as a small screen, which it is claimed is suitable for repeating some of the experiments described in the text.

Cours de Chimie. ("A Chemistry Course"). By R. DE FORCRAND. Paris: Gauthier-Villars. 1905.

THIS book provides a one year's course in the elements of chemistry, and it is difficult to discern in it any features for which it can be specially praised or blamed. It follows the old traditional lines both as regards arrangement and matter, and shows no signs of originality of treatment in any respect. The first volume, beginning with short sketches of some theoretical aspects of the subject, goes on to a descriptive account of the elements grouped together in families, while Volume II. treats of the rudiments of organic chemistry, and also includes a short course of analysis, which will probably be found the most useful portion of the book. It gives separation tables, and a scheme for the analysis of a salt and mixtures of salts, and a good chapter on quantitative analysis, volumetric methods being thoroughly well treated. Gas analysis is also included, and the ultimate analysis of organic compounds. As an intermediate course the book is at least unobjectionable, and it appears to be accurate in the information it gives.

Die Darstellung des Zinks auf Elektrolytischem Wege. ("The Electrolytic Preparation of Zinc"). By Dr. Ing. EMIL GÜNTHER. Halle-a-S.: Wilhelm Knapp. 1904.

ALTHOUGH the author of this monograph has a firm belief in the practicability of the application of the electrolytic method of preparing zinc, he is forced to acknowledge in the preface that the experiments aiming at the perfection of this method have so far met with but little success. After a brief period, during which electrolytic methods were subjected to much investigation on all sides, they have been practically neglected recently, and thus the greater part of the monograph is occupied with the discussion of processes which have never been of any technical importance. In the event, however, of its being found possible to work under such favourable conditions as to be able to compete with ordinary methods, this collection of the experiences of past investigators will no doubt be useful to those who wish to pursue the subject, and the accounts of the author's own work are very interesting. The Hoespfner

process, which is of special interest as being probably the only one in which metallic zinc can be prepared from aqueous zinc chloride solution, is treated at considerable length, and is taken as the basis for the calculation of the cost of working. This process has been worked both in Germany and in England with good results, and is consequently fully deserving of the special attention given to it in the monograph.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

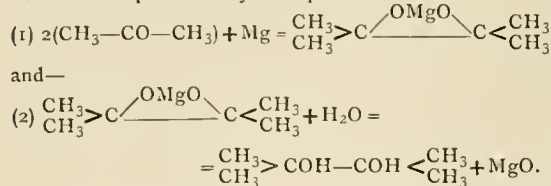
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxi., No. 11, March 13, 1905.

Atomic Weights of Hydrogen and Nitrogen. The Degree of Accuracy of their Determinations.—A. Leduc.—Taking oxygen as 16, the author finds the atomic weight of hydrogen to be 1.0076. M. Guye and Daniel Berthelot found respectively 1.00765 and 1.0075—numbers which are in perfect accordance with the above result, the fifth place of decimals practically having no value. For nitrogen the author's number is 14.005, as against M. Guye's 14.04. However, he believes that, by his purely chemical experiments, the atomic weight of nitrogen is less than 14.01.

Dextro-lactic Acid.—E. Jungfleisch and M. Godchot.—In a previous research M. Jungfleisch found that during the extraction of *d*-lactic acid from *d*-lactates, under certain conditions the *d*-lactic acid is transformed more or less completely into (*d*+*l*)-lactic acid. The authors now investigate the conditions under which *d*-lactic acid can be obtained free from (*d*+*l*)-lactic acid, using *d*-lactate of quinine for the preparation.

Action of Magnesium Amalgam on Dimethylketone.—F. Couturier and L. Meunier.—When magnesium amalgam acts on dimethylketone, the resulting reaction can be represented by the equations—



From these equations it seems that two molecules of acetone react with one atom of Mg, whilst, in reality, three molecules take part in the reaction. It appears that one molecule of acetone is fixed as an acetone of crystallisation, which is afterwards recovered in the mother-liquors of the pinacone hydrate as one of the products of the dry distillation.

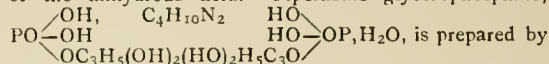
Oxethylcrotonic and Ethylerythric Acid.—M. Lespieau.—Oxethylcrotonic acid,—



is a solid white body, soluble in ether, ligroin, benzene, and alcohol, from which solvents it can be crystallised by evaporation. It melts at 45°, and boils at 145–146° under a pressure of 26 m.m. Ethylerythric acid can be prepared from this by the action of baryta and barium permanganate. It has the formula $\text{CH}_3\text{OC}_2\text{H}_5\text{—CHOH—CHOH—COOH}$, and melts at 90–92°. Saturated with the theoretical quantity of lime, it is neutralised, but an indefinable gummy product results.

A Method of Volumetrically Estimating Hydroxylamine.—L. J. Simon.—The author estimates the errors due to the titration of hydroxylamine with permanganate.

Piperazine Glycerophosphates.—A. Astruc.—The author uses for his experiments piperazine in the form of the solid hydrate crystallised with 6 molecules of water, and corresponding to the formula $\text{C}_4\text{H}_{10}\text{N}_2 \cdot 6\text{H}_2\text{O}$. To prepare the glycerophosphates he uses pure commercial glycerophosphoric acid containing 20 per cent of the anhydrous acid. Piperazine glycerophosphate,



evaporating on a water-bath an aqueous solution of 2 mols. of glycerophosphoric acid and 1 mol. of piperazine, until a syrupy mass is obtained. On desiccating over sulphuric acid for some days, the glycerophosphate is produced as a pasty transparent mass, slowly soluble in water.

MISCELLANEOUS.

Soil Inoculation.—Sir John Shelley has called the attention of the Bath and West of England and Southern Counties Association to recent experiments in the United States and elsewhere with reference to bacteria cultures for the inoculation of the soil with the view of enriching it in nitrogen, and moved:—"That the Board of Agriculture be asked, should the result of their investigation on soil inoculation be favourable, to arrange for distribution of the inoculating material to agriculturists." This was seconded by Mr. Gibbons, and, after some explanatory remarks by Dr. Voelcker, was agreed to.

A New Thallium Mineral.—The element thallium, discovered by Sir W. Crookes in 1861, has up to the present been known as an essential constituent of only two minerals, viz., crookesite, a selenide of copper and thallium, and lorandite, a sulpharsenite of the latter element. To these minerals a third must now be added in hutchinsonite, a new sulpharsenite from the Binnenthal, which also contains thallium as an important constituent. The crystallographic characters of hutchinsonite were described about a year ago by Mr. R. H. Solly, who, of late years, has been particularly successful in discovering new mineral species in the Binnenthal. At the time of its discovery very little in the way of chemical investigation was possible owing to the extreme scarcity of the mineral, but during the past year additional crystals have been acquired for the British Museum, and from these about 80 m.grms. of fairly pure material have been obtained for chemical analysis. Thallium is present (up to nearly 20 per cent), together with lead, silver, and copper, in combination with arsenic and sulphur. A full description of the mineral will appear shortly in the *Mineralogical Magazine*.—G. T. Prior in *Nature*, April 6, 1905.

Royal Institution.—The following are the Lecture Arrangements at the Royal Institution, after Easter:—Professor L. C. Miall, Fullerian Professor of Physiology, R.I., three lectures on "The Study of Extinct Animals"; the Rev. H. G. Woods (Master of the Temple), three lectures on "Velazquez"; Professor Sir James Dewar, Fullerian Professor of Chemistry, R.I., three lectures on "Flame"; Professor J. A. Fleming, three lectures on "Electromagnetic Waves" (the Tyndall Lectures); Professor H. Marshall Ward, two lectures on "Moulds and Mouldiness"; Dr. J. G. Frazer, two lectures on "The Evolution of the Kingship in Early Society"; and Mr. A. H. Savage Landor, two lectures on "Exploration in the Philippines." The Friday Evening Meetings will be resumed on May 5, when a Discourse will be delivered by Professor H. E. Armstrong, on "Problems Underlying Nutrition." Succeding Discourses will probably be given by Professor E. Fox Nicholls, Sir Charles Eliot, K.C.M.G., Professor J. W. Bruhl, Mr. George Henschel, and Sir William H. White.

Influence of the Nature of the Electrolytes and the Material of the Electrodes on the Formation of Ozone.—M. Kremann.—While Grafenberg has observed the formation of ozone with a potential of 1.72 volts, the author has not been able to detect it with a potential of 2 volts. We must look for the reason in the decomposing catalytic action exercised by platinum on ozone. To demonstrate the influence exercised by the electrodes, experiments were made with anodes of platinum, peroxide of lead, nickel, and gold; as electrolytes we used sulphuric and phosphoric acids and soda-lye. From tables and curves made we may conclude that:—1. In sulphuric solution peroxide of lead gives better results than platinum. 2. With a platinum anode we observe a maximum return of ozone, with a concentration of sulphuric acid of 4 molecules per litre (return 2.12 per cent). With binoxide of lead the proportion of ozone rises regularly with the strength of the acid. When we increase the dimensions of the anodes the influence of the concentration is considerably diminished. 3. All electrodes appear to act catalytically on ozone, but peroxide of lead is the compound having the least decomposing action. Sulphuric acid is the best electrolyte to use for the production of ozone. In the presence of phosphoric acid the best return is obtained with an anode of peroxide of lead; in the presence of chromic acid the use of platinum gives the best results. In alkaline solution, ozone is only formed at a low temperature and with a platinum anode. The maximum return is obtained with a solution of soda at 1 molecule per litre.—*Zeit. Anorg. Chem.*, vol. xxxvi., p. 403.

MEETINGS FOR THE WEEK.

WEDNESDAY, 19th.—Microscopical, 8. "On the Application of the Undulatory Theory to Optical Problems," by A. E. Conrady. Exhibition of Pond Life. Chemical, 5.30. "Complex Nitrites of Bismuth," by W. C. Ball.

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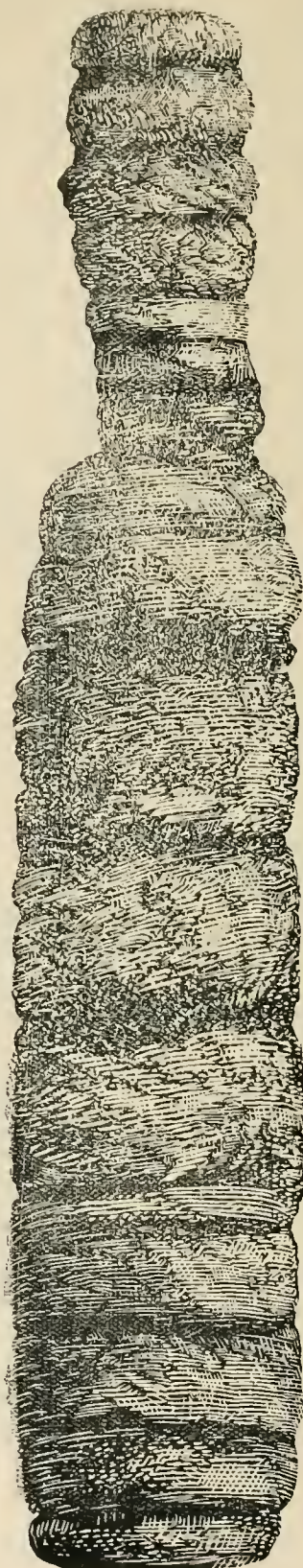
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THE CHEMICAL NEWS.

VOL. XCI., No. 2369.

THE SPECTROGRAPHIC EXAMINATION OF SOME THORIUM PREPARATIONS.

By G. EBERHARD.

I COMPLIED very readily with Dr. R. J. Meyer's request that I would examine spectrographically a series of thorium preparations made by him to discover if a separation of thorium into its supposed components had taken place (see CHEMICAL NEWS, vol. xci., p. 170); and I was the more pleased to do so because I had already been engaged on the examination of some thorium preparations of Drossbach, whose premature death is a loss to science. This renowned chemist had recently been investigating the decomposition of thorium, and he believed—in contradiction to his earlier views (*Zeit. Angew. Chem.*, 1901, No. 26)—that such a decomposition was possible. Unfortunately, neither notes nor spectral photographs which could throw any light upon his work on the subject could be found amongst his papers; but, on the other hand, a number of pure and impure thorium preparations were found, and these Frau Drossbach most kindly placed at my disposal.

Before I give my results, I must report shortly on the method I employed. The spectrograph used for making the tests was a concave grating apparatus (Abney's arrangement) made to my specification for the Royal Astrophysical Observatory by the firm of O. Töpfer und Sohn, Potsdam. By means of this apparatus, it was possible by one exposure to photograph on a film 85 c.m. long the whole spectrum of the substance to be examined, from λ 4800 to λ 2405. An ordinary arc light, with hand regulation, was used to vaporise the substance.

In all my work I did not use the spark spectrum, but only the arc spectrum, because for one exposure a much larger amount of the substance can be vaporised in the arc than is possible in the spark, and thus there is a better prospect of discovering small quantities of impurities. Moreover, the appearance of the lines of the spark spectrum is largely dependent upon the kind of electric excitation employed for the production of the spark, so that it is not easy to obtain such uniform results as when the arc spectrum is used.

As carriers of the substance to be vaporised I used good carbon rods, one end of which had been hollowed out to a depth of 8 to 10 m.m. These carbons were burnt shortly before using with a fairly strong current, until the chief impurities, especially iron and calcium, were so far distilled out that the spectral lines of these elements were either invisible or only faintly visible in a small pocket spectroscope. Then the substance to be examined was cautiously introduced into the little hole and vaporised by a direct current of 20 to 30 ampères (120 volts).

Besides the spectrum of this substance, that of iron was also photographed as a comparison spectrum, so that with the help of the known wave-lengths of the iron lines it was possible to determine the wave-lengths of the lines of the substance under examination correct to 0.02 to 0.03 Å.U. But if I wanted to examine, not a single preparation, but a series of fractions, I adopted a more convenient method, and photographed the spectra of these directly one under the other, without comparison spectra, so that any deviation among them could be seen immediately without measurement.

The results of the whole investigation were as follows:—The comparison of a thorium oxalate of Drossbach with Wyruboff's thorium sulphate, prepared quite differently, gave perfectly identical spectra; and, moreover, it was not

possible to discover in them the known lines of other rare earths (especially yttrium). Thus, these two preparations could be regarded as "spectroscopically pure," and their spectra could be used for comparison with the other preparations. Of such, the following were examined:—

Three thorium-magnesium nitrate fractions (crystals and mother-liquor) of Drossbach.

Drossbach's "most difficultly soluble thorium."

Five more of Drossbach's thorium preparations, not marked.

Fractions 1, 5, and 7 of Dr. R. J. Meyer's thorium fractionations by the chromate method.

Two of Dr. R. J. Meyer's thorium acetyl-acetone fractions (crystals and mother-liquor).

Three of Dr. R. J. Meyer's products of a thorium chloride sublimation by Baskerville's method (volatile, less volatile, and residue).

All deviations of the spectra of these preparations from one another, and also from that of pure thorium, could be ascribed to known impurities, so that there was no indication that a separation of the thorium into several components had taken place, or even begun.

The examination of thorium preparations from various minerals—thorite, fergusonite, yttrialite, uraninite (from Elvestad in Norway), uraninite (from Glastonbury in Connecticut*)—as well as that of a non-luminous thorium nitrate, also gave a negative result.

Finally, in order to obtain some idea of the sensitiveness of the spectral proof of the presence of impurities in thorium, I photographed the spectra of thorium oxide which was artificially adulterated with 0.5 per cent of the oxides of the yttrium earths, and thorium oxide which was artificially adulterated with 0.5 per cent of the oxides of the cerium earths. These adulterations were shown so clearly and well that there is not the least doubt that much smaller quantities of impurities can be detected.

From these experiments it may be concluded that, if the above-mentioned preparations were mixtures of the supposed components of thorium, the elements differing from the old thorium could be present in them only in quite insignificant quantity, as otherwise they would have been certain to be visible in the spectrographic exposures.

Meanwhile it must once more be emphasised that, at any rate on the ground of spectroscopic investigation, there is no confirmation of the alleged decomposition of thorium.—*Berichte*, 1905, xxxviii., 826.

A NEW REAGENT FOR ACONITINE.

By Dr. LUGENIO PINERUA ALVAREZ,
Professor of Chemistry of the Faculty of Science, Madrid.

THE alkaloid used for the research was pure crystallised aconite, "Gehe," from Dresden, Saxony.

In appearance it is a white, very brilliant crystalline powder. With the aid of a microscope the greater part is seen to consist almost entirely of hexagonal plates, derived from an orthorhombic prism by the modification of the acute angles, accompanied by small amorphous masses. It melts at 194°, changing into a yellowish red liquid which remains in a fused state some time.

By the action of concentrated sulphuric acid (D 1.84) at the moment the two bodies come into contact the alkaloid assumes a less intense orange-colour, and the solution is finally colourless.

By adding pure saccharose to the aconitine, and then sulphuric acid, the red colour which certain commercial aconitines assume when reacting upon the same bodies does not appear. It saponifies readily with an alcoholic solution of potash (KOH) in aconine and benzoic acid, without any observable production of veratric acid.

* I owe the last three preparations to the kindness of Prof W. I. Hillbrand, Washington.

By reacting with nitric acid ($D = 1.42$) on the alkaloid, and evaporating the solution to dryness in a salt-water bath, and then adding the alcoholic solution of potash, we did not observe the purple colour of the veratric reaction of pseudaconitine (*A. ferox anthora*, &c.). On gently heating the aconitine with medicinal phosphoric acid and with the viscous fluid, neither the red nor the violet colour was visible when using varying quantities up to 0.002 grm. of aconitine, recommended by Adelheim.

With the general reagents for alkaloids (Mayer, Wagner, Marmé, Dragendorff, Scheibler, Godeffroy, Schultze, Wornly, &c.) we observed no characteristic phenomena.

From all we have said above, it follows that the aconitine tested was almost pure, only containing very small quantities of amorphous bases.

And it also follows that, so far, we lack chemical reagents* which allow us to confirm the existence of this alkaloid in any case of analytical investigation, since those considered as characteristic are not applicable to pure aconitine, napaconitine, or benzoyl aconine, according to *A. napellus*.

After investigating numerous reactions according to different plans, we obtained the results mentioned at the end by exposing the alkaloid to the action of pure bromine, bromo-nitric acid, and of alcoholic potash, as follows:—

We submitted varying quantities (0.0005 to 0.0002 grm.) of the alkaloid, in a little porcelain crucible, to the action of 5 to 10 drops of pure bromine, slightly heating the mixture in a salt water bath to encourage the reaction.

We then immediately added from 1 to 2 c.c. of fuming nitric acid, and evaporated to dryness in the same bath, adding a little more bromine when the acid loses its colour, forming an oxidation product of a yellow colour. We then added 0.5 to 1 c.c. of a saturated alcoholic solution of potash, KOH, using pure ethyl alcohol ($D = 0.796$) for its preparation, and evaporated to dryness, obtaining a mass of a red or brown colour—more or less intense, according to the quantity of aconitine. The dish was allowed to cool, and then 5 to 6 drops of an aqueous 10 per cent solution of sulphate of copper were poured in, and, having well bathed the inside surface of the dish with the copper solution, we observed that the latter assumed a very deep green colour.

PRECIPITATION OF GOLD IN THE CRYSTALLINE FORM.

By ROBERT DYKES.

DURING the course of some experiments with uranium nitrate, UO_2NO_3 , a crystalline precipitate of metallic gold was obtained in the following manner:—

To about 5 c.c. of a saturated solution of uranium nitrate was added a similar quantity of auric chloride, $AuCl_3$. There was no apparent change observed even on standing for twenty-four hours. The solution, when evaporated to dryness over a water-bath, simply yielded an intergrowth of yellow crystals of uranium nitrate and auric chloride. The mixed salts were dissolved in ether, and evaporated down. As evaporation proceeded a smell not unlike methyl oxalate, $C_2O_4(CH_3)_2$, was given off, but the solution suffered no apparent change until reduced to small bulk. At this stage the solution changed from pale yellow to orange-red, and became viscous; on adding a few drops of distilled water and proceeding with the evaporation, a bright yellow scintillating precipitate formed, the solution again becoming viscous. The pre-

cipitate was removed after dilution with water by decantation. The particles being very minute took some moments to settle, and although heavy were easily disturbed.

On repeating the above experiment amorphous gold was obtained in one case and scaly gold in another, but on adding a few drops of auric chloride to the filtered solution and the evaporation being continued, a crystalline precipitate was formed. Another experiment only yielded the gold in crystals after repeated evaporation and the frequent addition of auric chloride.

Examined under the microscope the precipitate appears by reflected light to consist wholly of exceedingly brilliant metallic crystals, brassy yellow in colour. They are well formed, and vary in size from 0.01 m.m. to 0.05 m.m., the faces being very perfect. The crystals are all isometric forms, and under a high power by transmitted light appear translucent, are of a blue or green colour according to their thickness, and are isotropic between crossed nicols. They are insoluble in strong hydrochloric or nitric acids, but dissolve readily in aqua regia, yielding on evaporation deliquescent crystals of auric chloride, which, when treated with freshly prepared stannous chloride solution, give the characteristic purple of Cassius reaction for gold.

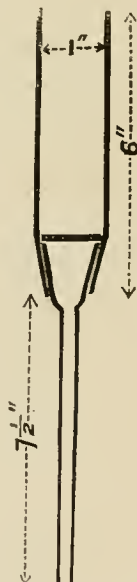
Experiments were made with uranium nitrate and auric chloride, also methyl ether and auric chloride alone, but the gold was only thrown down in the amorphous condition. That the reduction of the auric chloride is due to ether was proved by placing an ether solution of auric chloride in a sealed tube for some days in darkness. When examined, the sides of the tube were encrusted with very bright and perfect crystals of gold.

March 17, 1905.

A NEW FILTER TUBE.

By H. P. MASON.

THE filter tube shown in the sketch has been designed, and is used for, filtrations through paper-pulp and asbestos in metallurgical analyses.



In reality, the special characteristics which are of use, or have been employed, to distinguish between the alkaloid and all its analogues, are—its flavour, its crystalline form, its micro-chemical reaction (produced by iodohydrate of crystallised aconitine, suggested by A. Jürgens, of Dorpat), and, lastly, its physiological action (period of high pulsation). But all these characteristics are unreliable, of little use in ordinary analytical research.

The new feature is that the stem is separate from the body of the tube, and is ground in, so that it is held in position and forms a ledge on which a porcelain filter-disc can rest. A filter is prepared by closing the stem orifice

with a finger and half-filling the tube with water to displace the air; the disc is introduced, and the filtering medium poured in; the water is then allowed to flow out, and the filter made of the desired texture by means of a flat-headed glass rod. When a filtration is completed, the stem is loosened and raised slightly, when it empties itself of wash-water, and, being made slightly longer than the tube body, it can be used to eject the filter, which, in its passage down the tube, effectually removes and carries with it any particles adhering to the sides.

THE IMPORTANCE OF ACCURATE MEASUREMENTS AT VERY LOW TEMPERATURES.*

By Dr. H. KAMERLINGH ONNES.

(Concluded from p. 175).

To fulfil the conditions for the attainment of constant temperatures over the whole range below the freezing-point, is the task of the cryogenic laboratories.

He who enters a cryogenic laboratory will perhaps expect phenomena of intense cold to meet him. This is not the case. Thanks to the use of regenerators and walls of very small conductivity, the extremely low temperature in the apparatus will be generally the less perceptible at the outside, the better we have succeeded in producing the cold.

As to the arrangement itself, the most economical, and also in general the most rational and least complicated method, seems to me to have a cascade of cycles each with its own compressors and vacuum pumps, which reflect, so to speak, the history of the gradual production of the low temperatures. Though the compressors and vacuum pumps with their flapping belts, which remind one of a factory, may especially draw your attention, the centres of activity are the apparatus to keep up constant low temperatures, the *cryostats* (cf. *Communications*, &c., No. 83). The slightest variation of temperature therein is watched by the aid of electrical appliances, and from time to time signals are heard according to which the assistant modifies more or less the temperature of the liquid-bath (for instance, by means of the vacuum pumps).

For a physicist these cryostats are mere auxiliary appliances. He does not begin to acquire the knowledge at which he aims until his carefully prepared measuring apparatus are immersed into those cryostats, and others are connected with them. The problems which he has set himself render it necessary, as I expressed it twenty years ago, when I also took the consideration of the law of corresponding states as my basis, that the laboratory should be provided not only with the pumps of Cailletet and of Pictet, but also with instruments of precision which are treated like astronomical instruments.

The instruments which in the cryostats are brought to the required temperature must in most cases be especially constructed for this purpose. This is another reason why we cannot succeed in making accurate observations at low temperatures unless we devote ourselves entirely to it—unless we specialise.

Indeed the time is not far off when in all laboratories the physicists will choose a special line of investigation. The development of science has been rightly termed explosive by Wiener. Its course becomes more and more rapid; the number of students increases. Powerful nations, America foremost, are founding new universities. According to Lockyer, England wants eight new universities if it wishes to maintain its present position. Everywhere new laboratories are rising, fitted according to requirements never dreamt of before. Division of labour

is necessary everywhere; it is indispensable in our small kingdom, whose universities, deeply rooted in our national life, bear the proud device, "Je maintiendrai," written by princely hand; division of labour between our universities and our technical academy, not by regulations, nor even by mutual agreement, but in spirit.

As for me, I long ago learned to consider the ideal of a large Huygens laboratory at Leiden subordinate to the much loftier ideal that our Dutch physical laboratories together should represent the whole domain of physics. (See H. Kamerlingh Onnes, "De beteekenis van het quantitatief onderzoek in de Natuurkunde," Inaugural Oration, Leiden, 1882). And it is certainly more than the reflection of the sympathy and friendship which bind the Dutch physicists when I see this ideal being realised.

A laboratory arranged especially for low temperature research will gradually come to take a place of its own in this scheme.

The many-sided connection with all sorts of theoretical questions which extend over the whole territory of physics is not impaired by thus limiting the field of investigations to low temperatures. On the contrary, it seems that the path towards the solution of problems of the most different kinds lies through the cryogenic laboratory. And especially when we want to gain an insight into the more delicate structure of matter, and into the effect of forces exercised by the smallest particles.

The investigation of the equation of state itself is in the first place called upon to spread light on this subject.

Let us imagine ourselves for a moment in the world of the invisibly small bodies. Long ago various reasons led to the conviction that all bodies consist of molecules, which in a gas fly about with great speed. While moving to and fro, the molecules collide with each other and with the walls of the space in which they are enclosed, exactly as would be the case with a swarm of bees crowded in a limited space. The number of the molecules, their velocities, and the way in which the molecules behave in these encounters, determine the pressure on the walls. If all these data were available we could derive this pressure by a complicated though not impossible calculation; we could derive the equation of state for the substance in question.

It is much more difficult, with the observed equation of state as a basis, to gain some knowledge of the nature of the molecules and their mutual actions.

When we are placed outside a swarm of individuals unknown to us, and which we can neither see nor touch, we cannot estimate merely from the pressure exercised by them under different circumstances on the walls enclosing them, how many individuals form the swarm, what they look like, and how they behave in the collisions.

The difficulties apparently remain insuperable, even if we confine ourselves to putting questions which hardly enter into particulars about those individuals, although with the swarm as a body various experiments have been made which enable us to answer these questions. Mathematical physics does not, however, shrink from this task, and it can solve more problems according as experimental physics furnishes it with more data of the nature of the equation of state.

In order to answer the questions, it forms hypotheses, creates images which happily represent some properties of the mechanism of the unknown individuals or some results of intricate computations about these mechanisms, and with these the experimenters work on. Thus the simplest representation of a molecule is a hard, perfectly elastic sphere. With such representations as a basis, mathematical physics calculates the phenomena, and in the agreement with them it finds a test for its hypotheses. It has succeeded in deriving from the equation of state in the rarefied gaseous condition the fact that the molecules fly about with a speed often greater than that of a rifle-shot. The phenomena of viscosity have led Van der Waals to a count of the molecules and to the measurement of their mean dimensions, i.e., the radii of the spheres by which we

* Address delivered in commemoration of the 329th Anniversary of the University of Leiden. From *Communications from the Physical Laboratory at the University of Leiden*, Suppl. No. 9 to No. 85-96.

have represented them. He found that the dimensions of the molecules are so small that, when magnified some hundreds of millions of times, they would not appear larger than billiard balls, and their number is so large that a cubic centimetre of air contains several trillions of them. The obtained results, which are confirmed by other phenomena, do not probably diverge much from reality.

In consequence of a closer investigation of the equation of state in connection with the specific heat in the rarefied gaseous state, Van der Waals has considerably modified the image given above, and has brought into account the fact that the molecules in general are compressible. If the molecules of all normal substances were elastic spheres of corresponding compressibility, and if they exercised forces on each other in inverse proportion to a power of the distance between their centres, the law of corresponding states would hold rigidly. The deviations point either at differences of compressibility or at different forces, or at both.

Obviously we must first suppose again that the atoms which form the molecule are themselves perfectly hard elastic spheres, and that, for instance, a hydrogen-molecule consists of two such spheres which are connected as if by a spring. In molecules which can be separated by electrical discharge into two oppositely charged parts, the transformation which a molecule suffers by its collision with another will undoubtedly be connected with dielectric elasticity, and this transformation might be so great that the substance would no longer behave normally. Besides these actions emanating from their centres, molecules formed thus will perhaps exercise others which correspond to those of two small compass-needles brought together, and which might depend on properties in the solid state of the substances we have now in view.

The number of possible hypotheses, however, is indefinite. Therefore it will be of the greatest interest to find the way leading from the simple to the more complicated problems.

Thus the pith of the investigation of the compressibility and the actions of the molecules will before long become that of the simplest substances, *i.e.*, the monatomic ones; hence, as monatomic mercury can be observed only over a very small range of reduced temperature, we will have to turn to argon and the noble gases helium, xenon, neon, and krypton, which have been separated from the air by Ramsay.

Although their spectra are very valuable for the explanation of the Northern Lights—by discovering them Ramsay has brought this phenomenon within the walls of the laboratory as Newton brought the phenomenon of the Rainbow—the highest value of these costly substances consist in the fact that their equations of state are equations of state of the atoms themselves.

If the atoms are indeed incompressible and the forces which they exercise are central, the form of the equation of state for these substances will be the simplest. And at the same time the condition will be fulfilled for the validity of the law of corresponding states for these substances *inter se*; they will procure the fundamental model of which we have spoken before.

It is a tempting experiment to find out whether all this will be verified, and what would result from the investigation of mixtures of these substances for the interactions of the atoms. Moreover, these mixtures would also have to be investigated, and the theory of the free energy surface transmitted to the cryogenic laboratory, in order to correct for almost inevitable small impurities, which, especially near the critical state, grow in importance. (A great number of the *Communications*, &c., are devoted to the development of this theory; Nos. 4, 7, 8, 11, 13, 16, 17, 43, 45, 47, 55, 56, 59, 64, 65, 75, 79, 81, 88, Suppls. 3, 5, 6, 7, are all related to it). The way to the very interesting investigation of the equations of state of the monatomic substances sketched here, will be prepared by the investigation of the ordinary permanent gases in the cryogenic laboratory.

We are still very far from having considered in our representation of the atoms, and of the manner in which they constitute the molecules, all that could be derived from the mere investigation of the above-mentioned equation of state, which equation indicates the pressure for each condition, and is called the *thermal* equation of state, to distinguish it from other equations which indicate the relations of other properties to the state of the substance.

And what may not be learned if we shall take into account the phenomena of viscosity in all the conditions in which we have considered the thermal equation of state in the cryogenic laboratory (*cf. Communications*, &c., Nos. 2, 12); in other words, if we shall find one of the *thermokinetical* equations of state of the substance! What may not be learned if we shall study other properties, such as capillarity (*cf. Communications*, &c., Nos. 6, 18, 28, 32, 39), conductivity for heat, &c., in the study of which the path leading through the cryogenic laboratory will conduct us over and over again to an equally immeasurable and entirely untitled field of experimentation!

A still wider tract is opened up when we direct our view outside the realm of thermodynamics.

The problems of the mechanism of the atoms require numerous investigations at low temperatures of phenomena of quite a different character.

Suppose it had been proved that a mercury atom and a helium-atom were incompressible. It would not therefore ensue that the space occupied by those atoms must be considered as being entirely uniformly filled.

We rather accept the idea worked out by Lenard.

Lenard assumes that each atom consists of a number of particles; dynamids, which are more numerous according as the mass of the atom is larger, each being extremely small in comparison with their mutual distances, and composed again of two particles oppositely charged with electricity which go together like a planet with its satellite.

Every atom, according to our older representations the very minutest particle of one of our planets, would itself, therefore, be again a planetary system of dynamids floating in the world-ether.

Lenard's conception is founded on investigations about the behaviour of small electrically charged particles (much smaller than atoms), which, when driven by the discharge against the glass of a Röntgen tube, produced the green glow, *viz.*, the *electrons*, with which are for ever connected the names of Lorentz and Zeeman (Zeeman's research was published in *Communications*, &c., No. 33). When these electrons at the place where we observe the green glow are allowed to escape through a window of extremely thin aluminium foil cemented over a very small opening in the wall (prepared on purpose), and to pass into the middle of some gas, they enter into its atoms and stick in them, and this the more easily according as the weight of these atoms is larger and the velocity of the electrons is smaller. To explain this Lenard surmises that the dynamids are centres of relatively immense forces, and that by means of the latter they catch the electrons, as in our planetary system the sun and Jupiter catch the comets which come near them from the depths of the heavens.

The satellites of the dynamids themselves are also electrons. The free electrons may be called the comets of the atoms.

Liquid mercury must be conceived as consisting of densely crowded systems of dynamids. It conducts electricity because the free electrons, satellites which being torn from their planets have become comets, move from one atom to the other in the same way as we saw them just now force their way through the gas into the atoms. However dense the mercury seems to be, the scattered dynamids fill only an extremely small part of the space occupied by the metal. In this free space the electrons move like the molecules of a gas or a vapour, only impeded by their collisions with the dynamids.

Whether in a metal, when drawn in a certain direction, they will follow more or less easily depends on the time elapsing between two collisions of one and the same

electron with the dynamids, and hence on its velocity, which may be calculated exactly as if the electrons were gas-molecules, and on the forces exercised by the dynamids on the electrons.

When we lower the temperature, the speeds of the free electrons will diminish, and the collisions with the dynamids will occur less often. The result of this is that they can better obey an electric force, and the conductivity of the metal through which they move increases accordingly. For a moment it has seemed as if at absolute zero the conductivity of metals would increase infinitely, or at least to an extremely high value. By immersing conducting wires in liquid hydrogen, Dewar has found, however, that this is no longer probable.

We may account for this by observing the actions which the dynamids exercise on the electrons, especially on those which are deprived of their satellites. It seems as if the vapour of electrons which fills the space of the metal at a low temperature condenses more and more on the atoms. Accordingly, the conductivity, as Kelvin has first expressed it, will at a very low temperature reach a maximum, and then diminish again till absolute zero is reached, at which point a metal would not conduct at all, any more than glass. The temperatures of the maxima of conductivity lie probably sometimes lower than that of liquid hydrogen. At a much lower temperature still, there would not be any free electrons left, the electricity would be congealed, as it were, in the metal. As yet it does not seem possible to attain the temperature at which conductivity reaches a maximum, but the very great importance attached to observations of the conductivity of metals at extremely low temperatures (*cf. Communications, &c.*, No. 77)—where also investigations of the influence of small admixtures on the conductivity play a part—urges on to numerous researches, which may be said to lead to the equation of state of the electrons.

Besides, there is another means beyond the mere lowering of temperature for fixing electrons—for neutralising their comet-like character. The electrons have the curious property that under the influence of the magnet their orbits will deviate and will even curl themselves round the lines of magnetic force; and it was this property, on the strength of which Lorentz predicted the circular polarisation at the rims of Zeeman's spectral line, broadened in the magnetic field. Now, by placing a piece of metal in the magnetic field, conductivity is diminished, while at the same time a group of other phenomena appears in connection with the deviation of the orbits of the electrons, for the explanation of which the conception that the atoms consist of dynamids is important. Time forbids me to dwell upon all these phenomena in connection with magnetism (*cf. Communications, &c.*, Nos. 15, 19, 42, 48, 58, 61, 63, 72, Suppl. 2); it may suffice that I have pointed out the extensive field for measurements opened up by the magnetic, galvanomagnetic, thermomagnetic, thermoelectric equations of state, especially at the low temperatures at which the electrons are more and more fixed by the dynamids.

In order to learn anything about the forces exercised by the particles of the dynamids mutually, it will be preferable to subject a monatomic non-conducting substance, helium for instance, to electric forces. It will be necessary to determine the dielectric constant for each state of the helium, or, in other words, to determine the dielectric equation of state (*cf. Communications, &c.*, No. 52). And what holds for helium naturally holds also for all substances in different states of aggregation—including phenomena in crystals, pyro-, and piezo-electricity, another unlimited field for accurate measurements at low temperatures in which only a few points are known. These determinations will complete the thermal equation of state, and will be of the greatest interest, especially in substances with highly compressible molecules.

What we have considered thus far has shown that by exercising constraint with ponderable and imponderable means on the swarm of molecules, we have obtained data about the general structure of the molecules individually.

We have not yet, however, paid attention to the light vibrations which the molecules communicate to the world-ether—in the short time during which they travel over a distance about equal to their own length, a hundred times more numerous than the sound vibrations which the wings of a bee produce while it flies the distance of its own length.

And it is again the electrons in the molecule that produce these vibrations in the ether and absorb them from the ether as resonators. The travelling of light amidst these vibrating electrons cannot but yield invaluable data. The more so because we are able, by exercising constraint on the motions of the electrons, to modify the circumstances under which the light vibrations meet them. Therefore, we may reasonably expect important results, not only from the investigations of the refractive index, of absorption, dispersion, and fluorescence, but also especially from that of the light phenomena in the magnetic field. Besides the optical, the magneto-optical equation of state of a substance like helium will have to be determined in the cryogenic laboratory. Now we are glad when we succeed in the determination of the magneto-optical dispersion of oxygen, when it is compressed at ordinary temperatures, and when it is liquefied (*cf. Communications, &c.*, Nos. 7, 15, 24, 31, 46, 49, 57, 80, 90, Suppl. No. 1). Moreover, in speaking about light, this idea must be taken in the new sense it has acquired since it has been extended on the one side to the Röntgen rays, on the other side to the very slow vibrations of Rubens.

In whatever direction we turn our eyes, everywhere an immense amount of accurate unremitting labour is demanded of the cryogenic laboratories.

There is no doubt that before long we shall have to tread quite different paths from those now laid down. Radium with its curious properties points to this.

Are we to regard the radium-atom as a system of dynamids hurling forth its comets, i.e., the free electrons, with such force that at their entry into one of the molecules of air they make it burst into electrically charged atoms whose existence can be shown by the electroscope; the rebound of which force dissevers some of the planets of the system of dynamids and flings them out?

Do the particles of the emanation emitted by radium likewise fling electrons from their systems of dynamids with the same force as radium does? Is there any connection between emanation, helium, and radium which always occur together? Is emanation an explosive compound like ozone, which at a low temperature may be collected as an easily exploding liquid?

Are the phenomena of these substances connected with energy hid in the dynamids, or with a kind of energy which, still unknown, streams past us in the world-ether? Are the electrons themselves nothing but the expression of phenomena of motion in the world-ether, like the wave on the watery plain, which has no proper existence, but only expresses the rhythm in the circulating motion of the water particles? Nay, are perhaps the dynamids (perhaps substance itself) nothing else, and will the knowledge of the minute phenomena of motion in the world-ether reveal to us new sources of energy?

Undoubtedly, we are on the eve of great discoveries in physics which will revolutionise the whole of society. A presentiment of it stirs in the minds of physicists, and inspires them in their work. The faint light which indicates the presence of radium emanation condenses in a tube cooled with liquid air; this same light evaporates when heated and is led away by a gas. Will one of the first rays of the dawn of the future be caught in a cryogenic laboratory?

Heat of Formation of Oximes.—Ph. Landrieu.—The author determines in two different ways the heat evolved during the formation of oximes from aldehydes and acetones acting on hydroxylamine—one, directly, by the wet method; and the other, indirectly, by a determination of the heat of formation by use of M. Berthelot's calorimetric bomb.—*Comptes Rendus*, cxl., No. 13.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Annual General Meeting, March 29th, 1905.

Professor W. A. TILDEN, D.Sc., F.R.S., President,
in the Chair.

DR. A. E. H. TUTTON and Mr. A. G. BLOXAM were appointed Scrutators, and the Ballot was opened for the election of Officers and Council for the ensuing year. The President then presented the Report on the state of the Society during the past twelve months.

Mr. W. J. SELL moved the adoption of the Report; this was seconded, and carried unanimously.

Report of the Council.

The Council are glad to be in the position to report that the Society continues to flourish, and that, as measured by the number of papers read, its activity has exceeded that of any previous year.

On December 31st, 1903, the number of Fellows was 2700. During 1904, 128 Fellows were elected and 5 reinstated, making a gross total of 2833. The Society has lost 28 Fellows by death; 37 have resigned; the elections of 4 have become void; 52 have been removed for non-payment of subscriptions, and 1 Fellow has withdrawn. The total number of Fellows, therefore, on December 31st, 1904, was 2711.

The names of the Fellows who have died are:—A. H. Allen, F. E. Allhusen, J. Barclay, Sir I. L. Bell, F. B. Bengier, C. Beringer, H. N. Bilimoria, W. Chattaway, P. L. Dey, T. H. Dodd, W. H. Dodd, R. E. Doran, W. Francis, A. Gibson, C. G. Grenfell, H. Grimshaw, G. Housam, T. Isherwood, J. Jackson, A. Kitchen, J. Mason, D. Munro, T. A. Pooley, H. St. John, C. J. Sawyer, W. H. Stanger, R. M. W. Swan, and A. W. Williamson.

Among the Fellows removed by death, the Society mourns the loss of Prof. Alexander W. Williamson, who twice filled the office of President, and to whose initiative the publication of the *Abstracts* was largely due.

The number of Honorary and Foreign Members at the date of the last Annual General Meeting was 30. Six names were added to the list by the election on May 18th, 1904, of Prof. A. H. Becquerel, Prof. C. A. Lobry de Bruyn, Prof. F. W. Clarke, Madame M. Curie, Prof. C. Liebermann, and Prof. E. W. Morley. The Society has to lament the death of one of the newly-elected Members, Prof. C. A. Lobry de Bruyn, on July 23rd, 1904. The number of Honorary and Foreign Members, therefore, is 35.

During the year 1904, 215 scientific communications have been made to the Society, 188 of which have already been published in the *Transactions*, and abstracts of all have appeared in the *Proceedings*.

The volume of *Transactions* for 1904 contains 175 memoirs, occupying 1761 pages, whilst that for the preceding year contains 142 memoirs, which occupy 1490 pages.

The *Journal* for 1904 contains also 4617 abstracts of papers published mainly in foreign journals, which extend to 1920 pages, whilst the abstracts for 1903 numbered 3882 and occupied 1640 pages.

The abstracts for 1904 are classified in the accompanying table.

Owing to the great increase in the number of papers abstracted, it has become necessary to add to the editorial staff. Dr. C. H. Desch has been appointed Assistant Sub-editor, with the object of taking part in the preparation of abstracts for the press, and of relieving Mr. Greenaway of a portion of the clerical work.

Although an award of the Faraday Medal was made in 1895, fifteen years have elapsed since the delivery of the last Faraday Lecture. On April 19th, 1904, the Lecture

PART I.

Pages. No. of Abstracts.

Organic Chemistry 1072 1968

PART II.

General and Physical Chemistry .. 606

Inorganic Chemistry 541

Mineralogical Chemistry 132

Physiological Chemistry 501

Chemistry of Vegetable Physiology

and Agriculture 311

Analytical Chemistry 558

848 2649

Totals in Parts I. and II. .. 1920 4617

was delivered by Professor Ostwald in the Lecture Theatre of the Royal Institution, the use of which had been kindly granted by the Managers for the occasion. The subject of the Lecture was "Elements and Compounds."

The Wislizenus Memorial Lecture was delivered by Prof. W. H. Perkin on January 25th of the present year.

On the occasion of the celebration of the Jubilee of the Doctorate of Sir Henry E. Roscoe, a Past-President of the Society, on April 22nd, 1904, the Council welcomed the opportunity of sending an Address of congratulation to him.

Proposals have been received from the Chemical, Metallurgical, and Mining Society of South Africa, and from the American Chemical Society, for a reciprocal exchange of journals for members of each of these Societies and of the Chemical Society at a rate just sufficient to cover the cost of printing, addressing, and postage. After careful consideration, the Council were unable to accede to the proposals, as the effect on the finances of the Society could not be estimated, and a limit could not be set to the number of Societies which might seek the benefit of a similar exchange of journals.

The question of co-operation in the preparation of abstracts in English has been raised afresh by the American Chemical Society by the appointment of a committee to confer with the Chemical Society on this important subject. The Council have re-appointed the committee which discussed the possibility of co-operation in 1899, and await the proposals of the American Committee with every desire to consider their practicability.

Acting on the suggestion made in the Presidential Address at the last Annual General Meeting, the Council have arranged for the preparation and publication of a series of Reports on the advance made each year in chemistry. These reports will be issued early in each year, and it is hoped that they will prove to be of value, not only to the Fellows, but to students of chemistry generally.

Obituary notices of several deceased Past-Presidents have not as yet been published. These notices have now been received and are in type. Among them is included an obituary notice of Sir Edward Frankland, as the Council have been unable to obtain the manuscript of the Memorial Lecture delivered on October 31st, 1901.

A further increase in the use of the Library has to be recorded, 1057 books being borrowed during 1904, as against 991 during the previous year. The additions to the Library comprise 119 books (of which 67 were presented), 296 volumes of periodicals, and 52 pamphlets, as against 126 books, 271 volumes of periodicals, and 43 pamphlets last year. An alteration in the wording of Library Rule IV. has been made to enable new books to be borrowed at an earlier date than formerly.

The Society has been the fortunate recipient of the eudiometer used by the late Sir Edward Frankland in the analysis of ethyl in 1849, presented by Professor Frankland; of a bronze medal of Roger Bacon, presented by Mr. Oscar Guttman; and of an engraving of Berzelius, presented by Professor Retzius, of Stockholm.

A special Committee was appointed last June to revise

the By-laws, and reported in due course to the Council. The revised By-laws were submitted by the Council to the Society for consideration at an Extraordinary General Meeting on February 8th, but failed to secure acceptance, being referred back for further consideration.

A memorial, bearing the signatures of nineteen women engaged in chemical work, praying for the admission of women to the Fellowship of the Society, has been under consideration. The Council were advised that "married women are not eligible for election as Fellows of the Society; that it is extremely doubtful whether the Charter admits of the election of unmarried women as Fellows; that it would not be wise to elect even unmarried women without first applying for a supplemental Charter; and that the election of women as Associates would be legal after a modification of the By-laws expressly authorising their election." An alteration in By-law III. extending the privileges of the Associateship to women accordingly formed one of the changes in the by-laws recently proposed by the Council.

The third Report of the Joint International Committee on Atomic Weights, with its revised table of atomic weights, has been issued to the Fellows in the *Proceedings*.

Grants amounting in all to £215 have been made during the year from the Research Fund, and £26 16s. 6d. has been returned. Of the papers published in the *Transactions* during 1904, thirty-two were contributed by authors to whom grants had been made from the Research Fund.

The total income of the Society for the year 1904 was £6700 5s. 8d., and the expenditure £5982 14s. 6d.; in 1903, these were £6817 19s. 7d. and £5926 18s. 3d. respectively, so that whilst the income has fallen by £117 13s. 11d., the expenditure has risen by £55 16s. 3d. A glance at the balance sheet for 1903, however, shows receipts amounting to £257 which cannot be regarded truly as income from normal sources; in 1904 only £5 was so received. Allowing for these items, the income for 1904 shows an increase over that of 1903 of £134 6s. 1d.

The Treasurer's chief anxiety is due to the ever-increasing size of the *Journal* and the corresponding increase in cost. Both exceed those of 1903, the size by about 17 per cent. and the cost by about 10 per cent. the excess due to printing alone in 1904 amounting to £280 12s. 1d., whilst the total increase in cost reaches the large sum of £365 6s. 11d. Part of this is due to the fact that the January number for 1904 contained a double set of abstracts, thus leading to an increase both in abstractors' fees and printing, these two items really representing thirteen months instead of twelve. As pointed out by the President on resigning the Treasurership two years ago, the steady increase in the size and cost of the *Journal* seems to render it inevitable "that, in the near future, some more stringent regulations both as to the state of the manuscript and the dimensions of the papers will have to be imposed" if the Society is to carry on its work of publication efficiently. In addition to the cost of the *Journal*, there is in the present accounts a sum of £237 6s. for the printing of Vol. IV., Part 1 (Authors) of the Collective Index (1893—1902). On the other hand, there has been a saving of £42 14s. 5d. in the cost of the *Proceedings*. The Library has cost less by the sum of £150 13s. 3d., and the general administrative expenses, which in 1903 were abnormally high, owing to special circumstances, have fallen from £1138 5s. 5d. to £893 1s., a saving of £245 4s. 5d., notwithstanding the cost of introducing house telephones and also connecting the Society with the Post Office system.

The Treasurer reports that the new system of keeping the Society's accounts has been in full working order for two years and has been found most satisfactory in every way.

The Council desire to place on record their appreciation of the valuable services rendered to the Society by Prof. Wynne, and an expression of their regret that his removal from London obliges him to relinquish the office of Senior Secretary. By placing him among the Vice-Presidents, it

is hoped that the Society may continue to receive the advantage of his experienced co-operation in the work of the Council.

The TREASURER made a statement as to the Society's income and expenditure during the past Session, and proposed a vote of thanks to the Auditors, which was seconded by Dr. L. T. THORNE, carried unanimously, and acknowledged by Mr. E. GRANT HOOPER.

The PRESIDENT then delivered his Address, in which, after recapitulating the events connected with the Society which had occurred during the past year, he gave an exposition of his researches on the relation of specific heat to atomic weight in elements and compounds, the results of which led to the following conclusions:—

1. The influence of temperature on the specific heats of many elements and compounds is much greater than was formerly supposed.

2. There appears to be no one condition or set of conditions under which the law of Dulong and Petit is true of all the elements.

3. The nearest approach to a constant available for practical purposes is found by taking the mean specific heats of metals between the freezing- and boiling-points of water, recognising glucinum, boron, carbon, and silicon as exceptions, together with hydrogen, oxygen, nitrogen, and perhaps chlorine in the solid form.

It is possible that the atomic heats of elements in the gaseous state may be equal, direct experiment on the gases having led to the value 2.4 for hydrogen, 2.5 to 2.7 for oxygen, and 2.6 for carbon (in carbon dioxide).

4. The independence of each atom in an element or compound must be regarded as a fact of the utmost importance from the point of view of theory. That the molecular heat of a compound is the sum of the atomic heats of all the elements present is in harmony with the results of observations on other additive properties such as specific volume and specific refraction. Such independence suggests the idea that chemical combination results from the mechanical fitting together of atoms, so that a section through a mass would exhibit, if the atoms were visible, a certain tactical arrangement probably corresponding with the closest approximation possible under prevailing conditions. It has yet to be shown that chemical combination results, in all cases, from the existence of electric charges resident on the atoms or in electrons associated with them. The molecules of carbon compounds, especially, may be regarded as being probably formed by the adjustment of the constituent atoms to one another in respect to space, and it is noteworthy that the liquid binary compounds of carbon, the hydrides, chlorides, and oxides, are not electrolytes, and no case is known of the electro-deposition of carbon from such compounds in the elemental form.

Prof. RAPHAEL MELDOLA proposed a vote of thanks to the President, coupled with the request that he would allow the Address to be printed in the *Transactions*. Prof. G. CAREY FOSTER seconded the motion, which was carried by acclamation, and acknowledged by the President.

Prof. H. McLEOD proposed a vote of thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year. This was seconded by Dr. J. A. VOELCKER, and unanimously adopted. Prof. W. P. WYNNE responded.

The Scrutators then presented their Report to the President, who declared the following to have been duly elected as Officers and Council for the ensuing year:

President—Raphael Meldola, F.R.S.

Vice-Presidents who have filled the office of President—H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; A. Vernon Harcourt, M.A., D.C.L., F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.A., M.B., F.R.S.; W. H. Perkin, Ph.D., LL.D., F.R.S.; J. Emerson

Reynolds, Sc.D., M.D., F.R.S.; Sir Henry E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; T. E. Thorpe, C.B., LL.D., F.R.S.; W. A. Tilden, D.Sc., F.R.S.

Vice-Presidents—Horace T. Brown, LL.D., F.R.S.; Harold B. Dixon, M.A., F.R.S.; Wyndham R. Dunstan, M.A., LL.D., F.R.S.; David Howard; A. Smithells, B.Sc., F.R.S.; W. P. Wynne, D.Sc., F.R.S.

Secretaries—M. O. Forster, D.Sc., Ph.D.; A. W. Crossley, D.Sc., Ph.D.

Foreign Secretary—Sir W. Ramsay, K.C.B., LL.D., F.R.S.

Treasurer—Alexander Scott, M.A., D.Sc., F.R.S.

Ordinary Members of Council—Edward C. C. Baly; Augustus E. Dixon, M.D.; J. J. Dobbie, M.A., D.Sc., F.R.S.; Bernard Dyer, D.Sc.; Alfred D. Hall, M.A.; A. Lapworth, D.Sc.; J. E. Marsh, M.A.; E. J. Mills, D.Sc., F.R.S.; G. T. Moody, D.Sc.; W. J. Sell, M.A., F.R.S.; J. M. Thomson, LL.D., F.R.S.; J. Wade, D.Sc.

ANNIVERSARY DINNER.

The Anniversary Dinner of the Society took place at the Whitehall Rooms on Wednesday, March 29th, at 7 p.m., when the Fellows and their guests dined together.

The PRESIDENT, in proposing the toast of "His Most Gracious Majesty the King," said he did not intend to question the loyalty and the good sense of the Fellows of the Chemical Society and their guests by making a speech.

The toast was drunk with enthusiasm.

The PRESIDENT next proposed the toast of "Her Majesty the Queen Alexandra, their Royal Highnesses the Prince and Princess of Wales, and the other members of the Royal Family." No words, he said, were necessary to recommend the toast, but it would be appropriate to say on that occasion that they had all watched with interest the progress of the voyage undertaken by Her Majesty and her Royal daughters, and they trusted that they would return in due time from the sunny seas of the South refreshed and invigorated by the sea breezes.

The toast having been duly honoured,

Sir WILLIAM S. CHURCH, K.C.B., in proposing the toast of "Prosperity to the Chemical Society," said he did not know what may have been passing in the President's mind at the time when he (the speaker) was thought to be a fit person to propose the toast. It may have been that the President's memory went back to the time when few, excepting those of the medical profession, had any acquaintance with the chemistry of their day, and when few took any interest in the study of the phenomena of nature. When they looked round that assembly there could be no doubt of the position chemistry had taken in these days. That Society was one of the oldest of the Societies in the Kingdom, dealing with different branches of science. It was founded more than sixty years ago—in 1841—and as long ago as 1848 it received its charter. Just consider what had taken place since those days. At that time the Society numbered only 300 members. He did not know the present numbers, but what he did know was that the advances made in Chemical Science and the advantages to the world derived therefrom could not possibly be over-estimated. In that advance their Society had played a very large and prominent part. When one considered the extraordinary advance of knowledge which had taken place since 1841—and how the science of chemistry was now connected and inter-connected with all the ordinary necessities of life, it was remarkable to consider the difference between the position of Chemical Science in this country in 1841 and to-day. Out of their Society—which had for its object the advancement and the distribution of knowledge, and the publication of special researches in its own branch of science—had grown other societies—those which dealt with the application of chemistry to the arts and necessities of life. The principal societies were the Society of Chemical Industry, the Institute of Chemistry, the Society of Public Analysts, and the

Pharmaceutical Society. He did not know whether their Society had any titular god or goddess upon its sigillum or seal, but it must have been a difficult matter to make a choice, because they might have chosen Ceres as illustrating the peace and prosperity which had accrued to the country through the advances of chemistry; or, on the other hand, he feared they could equally have chosen Bellona when they considered how much chemistry had done in the promotion of arms. But neither of these objects had been the aim of their Society. Its true object had been the advancement of knowledge by searching out the forces and secrets of nature. What higher aim could a Society have? In those few words he gave them the toast of Prosperity to the Chemical Society.

The PRESIDENT, in replying, said he hoped they would agree with him that it was quite a proper thing to do to invite Sir Wm. Church, President of the Royal College of Physicians, to propose the toast, remembering that if chemistry did not spring entirely out of medicine, at any rate, the two branches of applied science had always been closely associated in the past. He was glad Sir William Church reminded them of the very important principle that experiment was the most secure basis of progress in all natural knowledge, which he thought was not always borne in mind by all his chemical friends. Some of them were ready to invent new hypotheses for explaining everything that occurred day by day, forgetting that every hypothesis, no matter how attractive, would sooner or later be superseded by something more comprehensive, based upon fresh knowledge. They had the honour of entertaining that evening one of the most brilliant exponents of the application of that principle—of course, he need scarcely say he referred to Lord Rayleigh. Experiment was the best foundation—he was looking to his friend Sir Wm. Ramsay to fully agree with him. Dr. Johnson once said that when a man knew he was going to be hanged in a fortnight, it tended greatly to concentrate his thoughts. They would, therefore, readily understand his own position during the past fortnight. That festival was the occasion of what might be called the apotheosis of the retiring President. He should wake up in the morning to find that he was no longer President of the Chemical Society, but one that had been President, and no matter what might happen in years to come, that great source of pride and satisfaction could not be taken from him. Many other changes also came about at the same time, and he could not help referring again with great regret to the change which deprived them of the help and the association of their friend Professor Wynne, the Senior Secretary. The Society owed a great deal to its officers, and especially to the Secretaries, and in welcoming Professor Crossley to fill the vacant post, they might feel confident that the share of the Society's affairs which fell to his lot would not suffer at his hands. The Society had now passed its youth, having celebrated its Jubilee fourteen years ago. Of course, as Sir William Church had reminded them, many changes had taken place, not only in the extent of their knowledge, but in the fundamental nature of their ideas with regard to all chemical questions since the foundation of the Society. Occasions like that must revive very vividly in the minds of some of the past presidents—several of whom he saw present that evening—the successive changes that had gone on since they held office. In the past year they had lost, in the person of the late Professor Williamson, a Past-President, one of those great men who had helped to lay the foundations of their science and of whom so few now remained. The Chemical Society had grown rapidly, but more particularly during the last ten or twelve years. He had been an officer of the Society for six years, and even in his time the membership had increased, roughly, about 200 per annum. When they entered upon the occupancy of the rooms which were allotted to them by the Government in Burlington House, the members in their ranks did not exceed about one-third of what they were now. That was thirty years ago. But now they were beginning to feel like some

of those crustaceans who periodically found their shells too tight. They wriggled out of it somehow and then grew a new shell better fitted to their enlarged proportions. They were not yet in a position to do that, but certainly the Society began to find its present quarters rather a tight fit. It seemed to him that a few informal gatherings for conversation, sometimes, perhaps, for demonstration and experiment, would be of great advantage to them; but he confessed he had never been able to see how it could be accomplished in their present quarters; and he could not help feeling some sentiment of envy towards their friends, the German Chemical Society, who occupied the palatial Hofmann-Haus in Berlin. They could hardly hope yet to secure quarters comparable with those. Nevertheless, the idea was fixed in his mind that informal gatherings might be useful in removing misunderstandings that sometimes would exist—notwithstanding the efforts of the Council and the Publication Committee—such as arose when authors of papers were not satisfied with the number of pages assigned to their important contributions. Questions of that kind arose, and occasioned now and then little heart-burnings—not very much—but even that little could probably be removed if they had opportunities of meeting together to talk—and to smoke, if they liked—and of getting to understand and to know one another rather better. The Fellows of the Chemical Society could really not be reproached for indulging too freely in conviviality. They dined only once in two years—and he was told that some of them drank beer after the ordinary scientific meetings—which, no doubt, occasionally were conducive to thirst. He was confident that the Society would continue to grow and prosper. It was necessary that it should grow, if they were to continue the development and publication of their splendid Journal. He would say fearlessly that their Journal—if not in bulk, certainly in quality, was equal to any scientific journal in the world—and it did, at the present time, fairly represent British chemistry. Of course, they must all go on reading French and German, but he wished some of their friends on the Continent could be induced to learn to read English—and the only way to compel them to do so was to make the Journal so good that they could not afford to ignore it. All this could only be accomplished by their sticking together, by doing their scientific best, and pouring into the Journal all the products of their laboratories and experimental work.

Professor RAPHAEL MELDOLA, F.R.S., proposed "Scientific Institutions." Looking at the list of institutions represented there that evening, he said, it might be confidently asserted that every one of the subjects represented by those institutions came well within the cognisance of the Fellows of the Chemical Society; and he supposed there was no branch of natural knowledge at the present time into which chemistry had not, in one way or another, inserted itself. They welcomed all co-workers in their domain. There were representatives of institutions other than those that had been mentioned, and he hoped Sir Thomas Elliott would allow the Board of Agriculture to be considered a scientific institution. Chemistry had certainly made itself felt in that department. They welcomed Professor Larmor, not only on behalf of the Society which he represented, but in his individual capacity. The great specialisation of science in modern times had taken away a great many of the communications which the Royal Society used to receive. This in no way detracted from the status or the importance of the Royal Society, but it rather spoke in favour of the active development of modern science in various directions. Professor Larmor's name stood pre-eminent in the great work of chemical science, although with regard to his own work, he (Professor Meldola) was afraid he must confess that he and many of his colleagues were not able to follow the Professor in all his abstruse flights. With regard to Dr. Glazebrook, they all knew that, although a comparatively young institution, the National Physical Laboratory had amply justified its foundation. He need hardly remind

those present that any institution which helped them to standardise the instruments they used, conferred an inestimable benefit upon their science and upon the work they were undertaking. Moreover, judging from a recent report of the National Physical Laboratory, much work had been done lately which might legitimately be classified as more or less chemical in character, and in welcoming the Director of that Laboratory they could only express their satisfaction that the results which had been achieved had been achieved with comparatively modest means, when they considered that the Government aid to the National Physical Laboratory was about one-fourth that given to the Reichsanstalt at Berlin, and one-fifth that given to the Bureau of Standards of the United States. In conclusion he paid a tribute to the work of Sir Norman Lockyer, Lord Rayleigh, and Sir William Ramsay.

Professor JOSEPH LARMOR, in replying, said he was glad to be greeted as an official of the parent Society, which had preserved the closest possible relations with her offspring. He believed that in this country there was a notion that much more could be achieved by the scientific workers here than in any other country in the world. Continental nations gave very extensive subsidies from public money, whereas in England it was considered that scientific men should provide their own means.

Dr. R. T. GLAZEBROOK also responded. He said his Institution had a large field to cover, and at each point of that field they were brought into close contact with other Societies. They claimed to be a kindred institution because they had the same high aims and employed exactly the same experimental methods as those pursued by the Chemical Society. He was glad to bear witness to the great assistance given them by their chemical friends, and the impossibility of conducting much of that work without that assistance, so cordially and generously given.

Sir WILLIAM RAMSAY, K.C.B., next proposed "The Guests." He said he would not be so invidious as to allude to their guests by name or qualification. These details could all be found in the "Dictionary of National Biography," or in the more modest "Who's Who." They were delighted to see their friends and guests present, and hoped to see them all again on many similar occasions.

The RE. HON. R. B. HALDANE, in responding, said he objected to be divided by a line, as Sir William Ramsay had done, from Professor Perry. If Professor Perry could, as Sir John Fisher once said, teach the differential calculus to the working classes he (Mr. Haldane) had ventured to teach equally dubious things to the working classes. He could not call himself a chemist, but he had got a conviction that the problem which lay in front of the British nation was how to develop what he might call the grey matter of the executive brain. All the things spoken of that night represented something new in the nation, and not only something new, but something of which they would have to see a great deal more if the nation was to hold its own in these days. Science counted for more than ever it did. The West had had a rude awakening at the hands of the East. The controversies which agitated the minds of politicians were of less importance than the great question of how to make the permanent element in politics more powerful and better than it was. He was not talking of Cabinets. They come and go, but to-day they seem to go more rapidly than ever. There was too little science in the present day, although one or two things had been done for which they were very grateful, in connection with the Navy and the Army, and the Defence Committee. That was one link. If they turned to the different departments of the Government there was hardly one which did not require science, if its policy was to be an effective policy. The War Office and the Admiralty were dependent on the higher problems at the command of science. The Department of Public Health—the Local Government Board—was in the same position, and so was the Board of Trade, which brought another kind of Science—that science which could only come from a very wide survey from the largest point of view of the dull subject of

statistics. Wherever they turned science was needed, and yet there was not sufficient attraction to a man of high attainments to put himself at the disposition of the State. Foreign Governments held out careers far in excess of any rewards and honours which the British Government could afford. Was it impossible to see an era in which the head of the Government could have at his disposition the first intelligence and the best brains which the nation could command? While that might be a dream, it was, he thought, a dream which events were preparing them for seeing realised. If we were to hold our own we must not be behind Berlin, the United States, or the French nation. There was a policy more worthy the consideration of politicians than some policies which were taking up the time of the House of Commons, and this policy had the great advantage that it was a non-party one. He looked forward to the day when somebody would put his back into this business, that somebody would have the power of so impelling the administration of the day that it would be forced to respond to the demand of every class of the electorate, and every section of British Society. Anybody who wished to attract public confidence could do worse than take up a policy of that kind, and he believed the British Treasury would open its hand. Science never stands still, and if science does not stand still, Governments cannot afford to stand still in their use of science. These were speculations which, perhaps, went beyond the moment, but he had a strong feeling that the time was very nearly, if not quite, ripe for them. They would see what was the mind of the nation on this point, and doubtless they would be subjected to the acute disappointment to which all were usually subjected when they formed great expectations. He hoped to see the position of science raised in the next few years, and he looked to the time when brute force would count for little, and knowledge for more.

Professor PERRY also responded.

FARADAY SOCIETY.

Ordinary Meeting, Tuesday, April 4th, 1905.

Prof. A. K. HUNTINGTON in the Chair.

Mr. A. H. HIORNS read a paper entitled "*Alloys of Copper and Bismuth.*"

The reading was illustrated by lantern-slides of the photomicrographic observations referred to in the paper.

This is further research on copper alloys carried out in a similar manner to that on the copper-arsenic series published in the *Transactions* of the Society, April, 1904.

Prof. Arnold has investigated the effect of bismuth, from 0.1 to 0.5 per cent, on copper, and found that the investing membranes surrounding the grains of copper appeared to be split down the centre, presenting a definite plane of cleavage. Dr. Gautier obtained a freezing-point curve similar to the author's, but his temperatures are generally higher.

The microscopic evidence mainly confirms the records of the freezing-point curves, of which there are four branches. We have pure copper and pure bismuth at the extremes, and solid solutions of copper in bismuth or bismuth in copper at intermediate points. The types of pattern on the etched surfaces depends on the position of the freezing-points on the curve. The eutectic-points occur at 243° C. and 1020° C., with a transition-point at 858° C. From this point with increase of bismuth in alloys containing 30 to 43 per cent of copper, the curve is practically a horizontal line showing little differences in the freezing-points. In this region two possible chemical compounds may be present, viz., Cu_2Bi_2 and Cu_2Bi , but there are no well-marked indications of such, either in the freezing-point curve or in the micro-sections. Such compounds can therefore only exist in contact with solutions containing excess of bismuth.

The above-mentioned transition-point is the transition-point between solutions of copper in bismuth and bismuth in copper, and at this point the two solutions have probably the same freezing-points, each being lowered by the addition of the other, thus forming a conglomerate of the two mixed crystals, which here exist in equilibrium.

Copper, with small percentages of bismuth, consists of polygonal grains, the boundaries of which contain a thin line of bismuthide. When such copper is broken the line of fracture follows this line. With 2 per cent bismuth the surface shows a characteristic eutectic structure. With increase of bismuth gradually widening boundaries to the grains appear and the interior is of a eutectic nature, which also increases with the addition of bismuth. With 57 per cent bismuth the whole surface is composed of grains of the two solid solutions, one of a light grey and the other of a light red colour. With 60 to 67 per cent bismuth the alloys are composed of the two solid solutions mentioned above, with the addition of dark blue grains, probably the compound Cu_2Bi . With 70 to 90 per cent of bismuth there are two main constituents, consisting of the red solid solution in a eutectic mixture. With 97.2 per cent of bismuth the whole is decidedly a eutectic mixture. The structure of alloys containing 98 per cent bismuth and upwards resembles pure bismuth.

The CHAIRMAN drew attention to the fact that previous observers had not noted the eutectic-point of pure copper and copper-bismuth solution at 1020° C., shown at D on the author's cooling curve. He hoped Mr. Hiorns would make his study more complete by systematically examining chilled alloys, as Heycock and Neville had done in the case of the copper-tin series.

Dr. C. H. DESCH remarked that the photograph of the 0.4 per cent bismuth alloy was the best that had yet been published.

Prof. E. WILSON thought that a further study of the 0.4 per cent alloy might throw some light on the well-known influence excited by bismuth in the conductivity of copper.

Mr. HIORNS, in reply to the Chairman, said that repeated experiments justified his belief in the existence of the eutectic at 1020° C.

The discussion was taken on the paper by Mr. E. KILBURN SCOTT, entitled, "*Refractory Materials for Furnace Linings.*" which was read on January 31st last.

The requirements of a good refractory material are as follows:—

1. It should be a poor conductor of heat.
2. It must be mechanically strong over a wide range of temperatures.
3. It must stand the reducing action of the charge; particularly of carbon.
4. If used in an electric furnace, it must be a non-conductor, even at high temperatures.

Refractory materials are classified as follows into four groups. The paper deals with the second and third groups, and particularly with the use of electric-furnace products as furnace washes over ordinary linings.

1. Carbon: for the highest temperatures.
- II. Silicon Carbides.

(a). *Carborundum* (crystallised silicon carbide, SiC).—This has established an excellent reputation as a furnace wash. The binding material mixed with the finely ground carborundum is silicate of soda, for washing ordinary fire-brick, or for coating iron, and fire-clay in the case of basic materials. Nothing but carbon—preferably charcoal—is known at present for use at temperatures above the decomposition-point of carborundum.

(b). *Siloxicon* (SiCO).—This is to a certain extent self-binding, but it is best to add alumina, and in certain cases non-alkaline clay, if desired to make up articles that can be baked before use, and if used for linings, either silicate of soda or coal-tar as binding materials; it is then baked in position. Siloxicon is very refractory, and inert in its

chemical action. It decomposes at 3000° C., forming silicon carbide.

- (c). *Amorphous Silicon Carbide*.—Being a fair conductor of heat, this is best used merely as a wash over ordinary fire-bricks, as should all silicon carbides. The best binding materials to use are glue, sodium silicate or gas-tar, according to circumstances, or the particles of carbide may be fitted together by surface oxidation.

III. *Crystallised Magnesite*.—Ordinary calcined magnesite brick is now recognised as the best material for lining basic open-hearth furnaces, cement kilns, &c., on account of its durability, freedom from moisture and silica, and resistance to corrosion. The native magnesium carbonate is usually calcined in a kiln, but the temperature is insufficient to shrink it thoroughly. The paper describes experiments made by the author in shrinking magnesite in some calcium carbide furnaces at Meraker, in Norway. It was possible simply to pass the magnesite down the chutes in the same way as the raw materials for making carbide of calcium. After a two hours' run with 3500 ampères at 65 volts, a block, about 15 inches cube, was obtained, which was practically pure crystallised magnesite. Thus to make 3 cwt. of crystallised magnesite took about 300 H.P. for two hours.

It has now been tested as a wash over the fire-brick lining of a carbide of calcium furnace, and it was found that the bricks lasted for two hundred hours without repair, whereas the unprotected bricks required repair after a five hours' heat. The author is of opinion that the crystallised material, without further preparation than being crushed to suitable dimensions, will prove of special value as a refractory material in metallurgical practice.

IV. *Ordinary Fire-bricks*, for the lower range of furnace temperatures.

Mr. H. N. DAINS (communicated) gave some comparative analyses showing the differences between Indian, Grecian, Styrian, and American magnesites. The great refractoriness of the first was due to the small amount of impurities it contained. Magnesite shrunk in the electric furnace certainly gave the most satisfactory results, and in support of this contention he quoted several striking instances. The principal use of burnt magnesite was for lining open-hearth steel furnaces, converters, rotary kilns for cement manufacture, furnace hearths, crucibles, and refractory bricks. The power-consumption given by the author was incorrect, because the experiment quoted was carried out on lightly calcined magnesite that had been lying about, and had taken up about 20 per cent of CO_2 and water.

Mr. F. GELSTHARP (communicated) said that if a material could be found to withstand the action of trisilicate of soda and lime at high temperatures, and at the same time would not oxidise, it would be a great boon to glass-makers. None of the materials mentioned by the author were suitable for the port-holes of tank glass furnaces.

Mr. W. MURRAY MORRISON hoped the author would furnish them with further more exact data regarding the temperatures the various refractory materials could stand, their mechanical properties, and their heat conductivities. Tar was the best binder to use for high temperatures, and the increase of conductivity it caused was unimportant; but something that would help the refractoriness of the material would be preferable.

Mr. L. GASTER said that a siloxen wash was insufficient for lining cement kilns, for example; hard bricks of the material were necessary.

Mr. R. CREMER found, after much experience, that silicate of soda was a perfect binder for carborundum. He considered carborundum as good a refractory material as any that had been described, and its mechanical properties were excellent.

Mr. R. S. HUTTON said that if magnesite were calcined in an electric furnace the CO_2 given off would rapidly consume the electrodes. But there was another "shrinking"

in the sense of increasing the specific gravity, and to this true shrinkage the valuable properties of magnesite (as of quartz) were due; this was best effected by fusion in an arc furnace, and Moissan had obtained a magnesite of specific gravity 3.65 in this way. In the author's experiments the magnesite was never more than in a semi-plastic condition; magnesite was easily melted in the electric furnace at something above 2000° C. Electric furnaces, contrary to what had been said, did not require such highly refractory linings as ordinary furnaces, because the material itself should be the effective lining. More information on the thermal conductivities of these materials was needed.

Mr. R. S. HUTTON and Mr. W. H. PATTERSON contributed a paper entitled "Electrically Heated Carbon Tube Furnaces." (Part I.).

(This paper will appear in an early issue of the CHEMICAL NEWS).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxi., No. 12, March 20, 1905.

Thermo-chemical Researches on Strychnine and Brucine.—MM. Berthelot and Gaudechon.—The authors thermo-chemically investigate strychnine and brucine, in order to complete their series of researches on the natural alkaloids, opium, quinquinas, &c. This series is as interesting from a purely chemical standpoint as from a biological one. The authors determine their heats of combustion, of formation from their elements, and of neutralisation by sulphuric and hydrochloric acids; also their multiple molecular state, &c.

Valency of the Hydrogen Atom.—M. de Forcrand.—The author investigates theoretically the consequences resulting from considering hydrogen as a divalent atom.

Diphenylamine Diazoamines. Derivatives of the Homologues of Aniline and Naphthylamine.—Léo Vignon and A. Simonet.—*o*-Naphthyl diazodiphenylamine can be prepared, but cannot be isolated in a pure state. *8*-Naphthylamine, previously diazotized, unites with diphenylamine under the same conditions, giving a reddish oil presenting the characteristics of the diazoamines. The following bases do not give diazoamine derivatives with diphenylamine:—The three monoaminophenols, *o*-amino-benzoic acid, and *o*-aminosalicylic acid. The results are negative, whether the method employed is that of simultaneous union and diazotation or previous diazotation.

Identification of Lactones by means of Hydrazine.—M. Blaise and A. Luttringer.—During the authors' researches on the migration of the ethylenic liaison in non-saturated acyclic acids, it was often necessary to detect the presence of lactones. After various unsuccessful experiments they found a very simple and very sensitive method of identification, which gave excellent results in all the cases examined. It consists in acting upon the lactone with hydrazine hydrate on a water-bath until all the water in the mixture is eliminated. On cooling, the residue solidifies to a crystalline mass, which is re-dissolved in a small quantity of boiling absolute ethyl acetate. In a short time the solution deposits crystals resulting from the union of a molecule of lactone with a molecule of hydrazine. The compounds thus obtained are extremely soluble in water and alcohol, but almost insoluble in absolute ether. They easily dissolve in absolute ethyl acetate at boiling-point, but are almost insoluble in the cold. These derivatives, to which the name of hydrazinolactones is given, are produced quantitatively, and possess a well-

defined melting-point, so giving a very satisfactory means of identifying the lactones.

Menthone Derivatives of Hexahydrothymols.—Léon Brunel.—The author examines the acetone obtained by the oxidation of the two thymomenthols. He foretold that the two thymomenthols would result in the same thymomenthone when subject to chromic oxidation. The substance produced, $C_{10}H_{18}O$, is a mobile colourless liquid having taste and smell identical with natural menthone. The density is 0.911 at 0°, and the substance boils without decomposition at 212° under normal pressure. It does not crystallise at -10°. It is very slightly soluble in water, but soluble in alcohol, ether, and acetic acid.

Bromo-acetal.—P. Freundler and M. Ledru.—The authors prepare bromo-acetal, $CH_2Br.CH<\begin{smallmatrix} OC_2H_5 \\ OC_2H_5 \end{smallmatrix}$, by direct bromuration of acetal in presence of calcium carbonate. To prevent decomposition they continually shake the mixture for several hours, and then treat it with an excess of hydrobromic alcohol. Under these conditions 100 parts of acetal give a yield of about 115 parts of the bromo-derivative which boils at 81–82° under a pressure of 27 or 28 m.m.

Action of Diphenylamine on Nitric Acid.—Isidore Bay.—Diphenylamine, when acted upon by nitric acid, gives an intense blue colouration, and this very sensitive reaction is considered as characteristic of the acid. As a matter of fact, this colouration is produced with a large number of oxidising agents, and even after exposure to the air for some long time. Diphenylamine, and more generally the aromatic amines, give strongly coloured products on oxidation. Such amines may be considered as playing the part of true leucobases with regard to their oxidation products, and form a new series of dyes which the author intends to further investigate.

MISCELLANEOUS.

Direct Synthesis of Nitrous Anhydride.—D. Helbig.—Up to the present we have never been able to prepare pure nitrous anhydride, this substance always decomposing into binoxide of nitrogen and hyponitride. The author conceived the idea of passing electric sparks through liquid air. These sparks were obtained from a Rhumkorf coil; the primary current was of about 8 or 9 ampères. The tension at the poles of the secondary wire was 1000 volts. The platinum poles became red-hot during the discharges, the liquid air became cloudy, and deposited greenish-blue flakes. About 0.5 grm. was obtained after one hour's action of the sparks on 300 c.c. of liquid air. Nitrous anhydride, in suspension in liquid air, has the appearance of the hydrated precipitate of Cr_2O_3 ; it fuses at -111° into a deep blue liquid; re-solidified in liquid air it retains this colour. It decomposes at about -100° into NO_2 and NO .—*Gazz. Chim. Ital.*, vol. xxxiii., [1], p. 454.

The Reaction between Yellow Phosphorus and Copper in Aqueous Solution.—Walther Straub.—Yellow phosphorus when plunged into an aqueous solution of sulphate of copper rapidly becomes black, then red. The red deposit is reduced copper. The blackish layer always found between the deposit of copper and the unattacked phosphorus is formed of a phosphide of copper. The solution contains phosphoric acid and free sulphuric acid. The ratio between the weight of the phosphorus that has reacted and the quantity of sulphate reduced, remains constant during the whole time that the reaction is unfinished, or when operating out of contact with the air. One molecule of phosphorus precipitates 2 molecules of copper from its solution. The oxygen necessary for the formation of PO_4H_3 is furnished by the water. The mechanism of the reaction is not known, but it is probable that the phosphide plays an important part. The copper reduced in the presence of an excess of phosphorus does not become oxidised. On contact with the air it seems

probable that the oxygen absorbed is used for the oxidation of the phosphorus. With very dilute solutions of sulphate of copper we do not observe any deposit of copper. With a concentration of $1/10^4$, the copper is deposited well crystallised; with $1/10^5$ we observe only a deposit of phosphorus; with a concentration of $1/10^6$ there is no longer any reaction. The author has observed entirely analogous results by placing phosphorus and metallic copper in water, in the presence of atmospheric oxygen. The phosphorus becomes covered with a layer of phosphide, which can be transformed into metallic copper if the experiment be sufficiently prolonged; the solution contains phosphoric acid. Other experiments enable the following explanation of the phenomena to be offered:—The phosphide formed is dissolved by oxidation (phosphate) (atmospheric oxygen). The soluble compound of copper is reduced by the phosphorus, which passes again into solution, and at the same time metallic phosphide is re-formed. Thus the phosphide becomes the carrier of the oxygen. Under these conditions, we must admit that the system $P + SO_4Cu + H_2O$ is only a particular phase of the preceding case, the oxygen, from the commencement of the experiment, being furnished in excess by the sulphate of copper instead of being borrowed from the oxygenated compounds of phosphorus, themselves formed in the presence of the atmospheric oxygen. When, in the system $P + SO_4Cu + H_2O$, all the copper in solution has been reduced, the oxidation continues, but only in contact with the air, as in the system $P + Cu + H_2O + O$.—*Zeit. Anorg. Chem.*, vol. xxxv., p. 460.

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The amount of material which can be used under the

preceding conditions is very restricted—as a trial I made tubes of 20 to 25 m.m. in diameter and about 30 c.m. capacity. The tubes terminated in capillary ends capable of being joined and sealed. I ought to remark that I had not much satisfaction with these tubes, as they were not regular and their thickness not uniform. This circumstance obliged me to reduce the pressure of the gases at ordinary temperature to one-third or even one-fifth of the pressure required if the tubes were regular and of diameter about 10 m.m., in order to avoid explosions. In all cases it is necessary to guard against the impurity of the silica employed, which often may contain perceptible quantities of alkalis which increase the fusibility and lessen the durability.

The best method of heating the quartz tubes is by the electric current in the ordinary way. These are placed in large tubes of unglazed earthenware, surrounded by a thin layer of platinum in spiral form. The air penetrates freely to the inside of this large tube. The current can be regulated by means of resistances; about 25 amperes is a convenient current to use at a temperature determined with a Le Chatelier regulator, or some other exact instrument. The temperature is kept constant for several hours. It is not advantageous as a rule to prolong the heating on account of the permeability of the silica, which property apparently develops with heat. The quartz tube introduced into the earthenware vessel is surrounded by a thin piece of platinum foil not communicated with the electric current, in such a manner as to avoid contact with the large tube. If, however, the temperature exceeds 1400°, the platinum foil comes in contact with the earthenware tube, as the silica tube begins to swell under the pressure of the gas. If this pressure becomes too great the little tube explodes; this breaks the big vessel and spoils the whole apparatus. It can, however, be reconstructed.

At the end of the experiment the whole apparatus can be left to cool slowly. It is, however, often preferable to extract the silica tube and the platinum foil which surrounds it by means of a platinum wire, fixed beforehand. The cooling can then be rendered instantaneous by plunging the tube, red-hot and enveloped in platinum, into a vessel of distilled water, preserving the contents as produced at the maximum temperature. The tubes behave satisfactorily under such conditions, and can be used for the solution of certain important problems in chemical mechanics.

It is best first to examine the silica tube and its contents before opening, with a lens or a microscope.

The gases should then be collected over mercury, measured, and analysed. For this purpose the cooled tube is held in the hand and immersed in a large vessel of mercury point downwards, and the point carefully broken off with a sharp file. The mercury gradually rises in the tube to a definite height, depending on the original pressure and the volume of the newly formed gas. The tube is then inverted under a small burette filled with mercury, and by methodical and prolonged shaking the whole of the contained gas can be transferred to the burette.

The silica tube, which is now full of mercury, can be weighed in order to determine its exact capacity.

On the other hand, the extracted gas can be measured by means of small graduated tubes 5 to 2 c.c. capacity, divided very exactly into hundredths of cubic centimetres, and so allowing of readings to cubic millimetres. I have already described the method of construction and accurate graduation of such tubes (*Ann. de Phys. et de Chem.*, Sixth Series, vol. xiv., p. 279). These gases are finally accurately analysed—a determination of the CO₂, O, CO, H, CH₄, and N being made by the recognised methods.

As to pre-existing solid substances or those formed during the experiment, such as the diamond or carbon separated from the hydrogen carbides, they may be extracted from the tube when the mercury enters and examined. Further, it is often useful when simultaneously heating two silica tubes placed in the same earthenware

vessel to examine the gases in one case and the solids in the other, the latter then not coming first in contact with the mercury.—*Comptes Rendus*, vol. cxi., No. 13, p. 104.

THE ACTION OF ULTRA-VIOLET LIGHT UPON GLASS.

By FRANZ FISCHER.

IN order to investigate the effect of ultra-violet light upon glass, I exposed the latter to the radiation of a quartz-mercury lamp of special construction.* The pieces of glass were brought very close to the quartz wall, without, however, touching it. The thin layer of air between quartz and glass was occasionally replaced by hydrogen, and the pieces of glass, which were sometimes heated to nearly 200°, were exchanged for glass tubes with water running through them; in both cases the result was essentially the same. The potential of the lamp varied between 17 and 18 volts; for this reason and in consideration of the nature of the vacuum in an incandescent mercury vapour lamp, the results obtained could not be ascribed to cathode or Röntgen rays, but only to ultra-violet light.

Eight different kinds of glass were exposed to the radiation of the lamp. Of these four remained outwardly unchanged, while the other four were coloured a decided violet within twelve hours, the beginning of the colouration being visible after only a quarter of an hour.

The following kinds of glass became coloured:—

1. Ordinary Thüringer glass.
2. Apparatus glass, from Greiner and Co., of Stützerbach, in Thüringen.
3. Apparatus glass, from Bock and Fischer, of Ilmenau, in Thüringen.
4. Normal thermometer glass, from Schott and Co., Jena.

And the following remained uncoloured:—

1. Jena combustion tubing, Schott and Co., Jena.
2. Durax glass, Schott and Co., Jena.
3. German lead glass.
4. English lead glass.

It could easily be shown by the analysis of the glasses that those which become coloured contained manganese (green manganate melt), while the others were almost entirely free from it.

Sir William Crookes (meeting of the Royal Society on Jan. 26th, 1905) has recently made a communication concerning pieces of glass which gradually became violet in sunlight at Uyuni (Bolivia), about 4000 metres above the sea. These glasses also contained manganese; the mixture of ferric and manganous silicate present in them under the influence of the sunlight, rich in chemically active rays at that altitude, passes into a mixture of ferrous and manganic silicate. The latter is violet, and the colour of the glass is due to it.

The explanation given by Sir W. Crookes may also hold for the colourations I observed; for all the specimens of glass which became coloured contain manganese, and the radiation of the quartz mercury lamp is rich in chemically active ultra-violet light.

The colour in my specimens of glass rapidly disappears if they are heated till they soften, and can be again produced after cooling by renewed exposure to the radiation. By covering parts of the pieces of glass with thin sheets of mica, I have proved that the colouration is due to an effect which is produced by that part of the radiation which has a short wave length. The glass underneath the mica remains uncoloured and the mica itself seems unchanged. Violet colouration of the glass is visible when Röntgen

* I shall shortly describe the construction of the lamp in the proper place.

tubes are used, and it might also be ascribed to the action of the ultra-violet light in the interior upon the glass which contains manganese. Perhaps the violet colouration produced by radium rays is connected on the one hand with the manganese in the glass, and on the other with a short wave length radiation arising either primarily or secondarily.—*Berichte*, 1905, xxxviii., p. 946.

A NEW RADIO-ACTIVE ELEMENT, WHICH EVOLVES THORIUM EMANATION.*

(PRELIMINARY COMMUNICATION.)

By O. HAHN, Ph.D.

(THE material for this investigation was provided by Sir William Ramsay; it was the final residue remaining after fusion with bisulphate of 5 cwts. of the cubical ore from Ceylon, for which the name "thorianite" has been suggested by Professor Dunstan. This residue was fused with carbonates, the silica was removed, and the carbonates dissolved in dilute hydrochloric acid. Lead was precipitated as sulphide, and the carbonates again precipitated. These preliminary operations were carried out by Mr. Charles Tyrer and by Dr. Denison).

This residue weighed about 18 grms., and a preliminary estimation of radio-activity led to the belief that it would yield about 15 m.grms. of pure radium bromide. The carbonates were dissolved in pure aqueous hydrobromic acid, and the bromides fractionated according to Giesel's method. But difficulties were soon encountered; the more soluble portion did not fall off in radio-activity, but gradually grew more strongly radio-active; the radium concentrated at the least soluble end, and the middle fractions become relatively weak in radio-activity.

Small traces of iron and other impurities, unavoidable in London, collected in the more soluble portions, and the ferric bromide imparted to them a brownish yellow colour. These, and indeed all fractions, were again treated with hydrogen sulphide, and a minute quantity of a peculiar dark brown precipitate came down. It was also radio-active; it was soluble in nitric acid to a pale green solution, and on evaporation crystals of two kinds deposited; easily soluble green crystals and less soluble white ones. The investigation of these bodies is still in progress.

By a series of troublesome operations, a quantity of precipitate was obtained by aid of ammonia, and to separate iron, it was treated in acid solution with ammonium oxalate; this produced about 10 m.grms. of crystalline precipitate, which was by far the most active preparation obtained, and which shows after two months no diminution in its radio-active power. It glows feebly in the dark, and imparts bright luminosity to screens both of platino-cyanide and zinc sulphide. If a current of air be blown through a solution of this substance and directed on to a screen coated with zinc sulphide, luminosity is produced, which, nevertheless, is different in intensity from that shown when a similar experiment is performed with Giesel's emanium. The phenomena are not so brilliant as those obtained from a strong sample of emanium kindly sent by Professor Giesel. It was not possible to perform the beautiful experiment of allowing the emanation to pour down on the screen and blowing it away, probably because the new substance emits β -rays in too great abundance. But that the dry substance also evolves emanation was easily discovered by help of an electrometer.

The first impression, that the new substance was identical with actinium or emanium, was found to be untenable,† for the new preparation evolves an emanation

identical with that of thorium; different samples gave for the half-period of decay from fifty-two to fifty-five seconds; for the half-period of the induced activity, somewhat more than eleven and a half hours was found, and a small remaining activity persists and decays very slowly. (The half-period for thorium emanation was found by Le Rossignol and Gimmingham to be 51·2 seconds—*Phil. Mag.*, July, 1904, p. 107; Bronson, working in Rutherford's laboratory, found 54 seconds). As this phenomenon has up till now not been noticed with thorium emanation, it may be conjectured either that another radio-active substance is mixed with the new body in very small traces, of which the induced radio-activity must have a long period of decay, or what is less probable, that the induced activity of thorium, like that of radium, changes into another product with a long radio-active existence. It is certain that radium emanation and also Rutherford's radium-E were absent.

The oxalate, which weighed 10 m.grms., dissolved in hydrochloric acid, gave a quantity of emanation considerably greater than would be evolved from a kilogram of thorium in solution; consequently, it is more than 100,000 times as active as thorium. Further work has resulted in the accumulation of 20 m.grms. of material nearly 250,000 times as active as its own weight of thorium nitrate. Thorium itself, if present at all, must be there in minimal quantity, for the oxalate gives tests for calcium for the most part. Whether this active substance is a constant radio-active constituent of thorium preparations, or whether it is another new radio-active element, remains still undecided. Its quantitative extraction from thorium salts has not yet been investigated. After precipitation of a small part of the solution in hydrochloric acid of the original ammonia precipitate with ammonia, the filtrate shows considerable radio-activity, which rapidly falls off in a few days, but does not wholly disappear, and the removal of this substance does not diminish appreciably the radio-activity of the insoluble residue. Whether that is due to thorium or not has not yet been quantitatively investigated. The close relation of the new body to thorium is proved, not merely by the apparent identity of the two emanations, but also in its having been separated from a mineral unusually rich in thorium.*

We are in hopes that it may prove possible, by several processes of concentration, to obtain an even more strongly radio-active product, and to be able to describe more in detail the chemical properties of the substance; one difficulty consists in the adhesion of the substance to all precipitates; all filters are radio-active, and can hardly be purified by repeated washing. The activity of the sulphide precipitate may, perhaps, be due to this cause; the emanation which it yields appears to be identical with that obtained from the precipitate with ammonia.

Recent researches would appear to show that this substance is present in soil in amount comparable with, but still considerably smaller than radium. G. A. Blanc has described in a paper on "The Radio-Activity of Mineral Springs," a gas which contains thorium emanation (*Phil. Mag.*, vol. ix., pp. 148 to 154); N. M. Dadourian, in investigating the radio-activity of subterranean air, has detected not only radium emanation, but also that of thorium (*Am. Journ. of Science*, 1905, vol. xix., pp. 16 to 22); and Elster and Geitel have described a preparation obtained from the mud from the Baden Baden "Ursprung" as containing no thorium in detectable quantity, but yet evolving thorium emanation in amount such that half a gramme of thorium oxide would be required to produce it. ("Radiaktivität der Sedimente der Thermalquellen," *Chem. Centralbl.*, 1905, vol. i.) They conjecture, therefore, the presence of a new radio-active element. Attention may also be called to the fact that inactive thoria is said more than once to have been obtained.

It is almost certain that all these emanations are the

* A Paper read before the Royal Society, March 16, 1905.

† The measurements of the emanations and excited activities were carried out in collaboration with Dr. Sackur, working in this laboratory; we also re-determined the half-period of decay of the emanation from Giesel's emanium as about three seconds, and for its induced activity a period of about thirty-six seconds. More exact measurements are in progress.

* Experiments are in progress in this laboratory to attempt to concentrate the radio-active substance from a large quantity of thorium; but, so far, no definite results have been obtained.

product of this new substance, and are not derived from thorium itself, for the amount of emanation obtainable from thorium is so small that, if it can be measured at all, it should be possible to detect thorium analytically in the source from which it is evolved.

APPARATUS FOR HEATING SUBSTANCES IN A VACUUM AT CONSTANT TEMPERATURES.

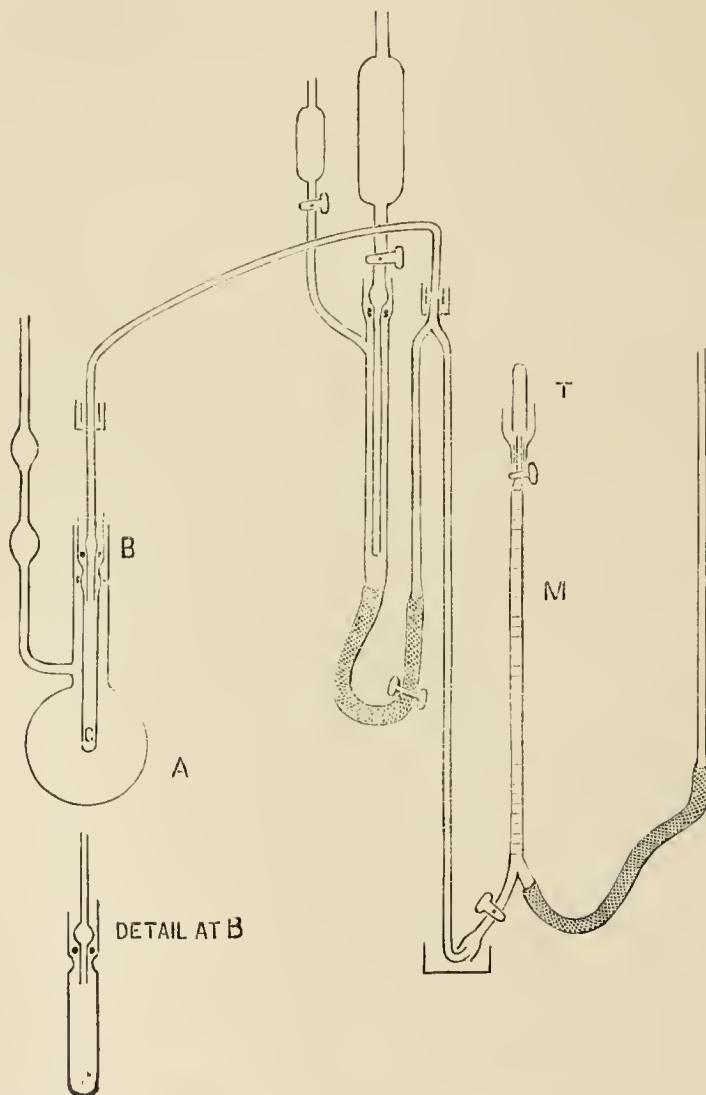
By Dr. W. R. HODGKINSON and A. H. COOTE.

THE apparatus here shown has now been in use for about three years for "the stability test" for gun-cotton, &c., and also for studying the rate of decomposition of salts or

the open end, so that the rubber ring is tightly wedged as the vacuum is made. We find that when a few drops of glycerin are put over this rubber ring a vacuum may be maintained for several weeks.

When employed for testing gun-cotton or similar substances, the whole of the heating vessel is surrounded with a wire gauze screen. The measuring vessel M is graduated in c.cs. and tenths, and, as is apparent, the volumes of gas collected may be measured from time to time by turning off the bottom tap and levelling up with the side tube. The gases may also be caught in the short tube T for analysis. The measuring tube M may contain either mercury or water.

Woolwich.



compounds when heated to some particular temperature. The sketch almost explains itself. A is the heating vessel, which may contain some liquid of constant boiling-point, so that the substance contained in the tube c may be heated in its vapour.

The tube c is a long test-tube drawn in slightly near

Retrogradation of Artificial Starches.—E. Roux.—The author investigates the retrogradation of artificial starches—(1) under the influence of water alone, (2) under the influence of acids and bases. He also examines the influence of heat on retrogradation.—*Comptes Rendus*, cxl., No. 14.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MARCH 31ST, 1905.

By SIR WILLIAM CROOKES, F.R.S.,
and
SIR JAMES DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, April 10th, 1905.

SIR,—We submit herewith, at the request of the Metropolitan Water Board, the results of our analyses of the 247 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the Metropolitan Water Board taking their supplies from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from March 1st to March 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 247 samples examined by us during the month, all were clear, bright, and well filtered.

In spite of the heavy rainfall during March, there is still a deficit on the first three months of this year. The actual rainfall recorded at Oxford was 2.96 inches; the average fall for the month is 1.47 inches; this gives an excess of 1.49 inches, which, if subtracted from the previous deficit of 2.71 inches, leaves a deficit of 1.22 inches, or 22.8 per cent on the thirty-five years' average.

Our bacteriological examinations of 429 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 630 others from special wells, standpipes, &c., making 1059 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 27 samples) ..	152
New River, filtered (mean of 80 samples) ..	3
Thames, unfiltered (mean of 26 samples) ..	8078
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 215 samples) ..	6
Ditto ditto highest	431
Ditto ditto lowest	0
River Lea, unfiltered (mean of 27 samples) ..	195
River Lea, from the East London District clear- water wells (mean of 27 samples) ..	3
Kent District, from the wells at Deptford (mean of 27 samples) ..	9

Of the 349 daily samples taken from the general wells of the Metropolitan Water Board, eighty-six samples, or 24.6 per cent, were sterile. One sample only, or 0.28 per cent, contained more than 100 microbes per c.c., viz., 431. In February eight excess samples contained an average of 138 microbes per c.c.

During the whole of our experience of the London waters for this period of the year, we have not known the bacteriological and chemical quality of the supply to be so good as it has been during the past month. In spite of the heavy rainfall, the purification effected by storage and filtration has been satisfactory.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, April 6th, 1905.

Prof. R. MELNOLA, F.R.S., President, in the Chair.

IT was proposed by Prof. ARMSTRONG and seconded by Dr. LAPWORTH that the minutes of the previous meeting be taken as read. After some discussion, the President ruled that the course prescribed in By-law XI. be followed.

MESSRS. B. M. JONES, C. E. FAWCITT, A. ANGEL, and W. H. RATCLIFFE were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Albert Edward Andrews, 37, Oakhurst Grove, East Dulwich, S.E.; Francis George Belton, 16, Clarkson Street, Sheffield; Edward S. H. E. Brettell-Vaughan, The Cwm, Aston-on-Clun, Salop; Thomas Walter Firth Clark, 117, Clerkenwell Road, E.C.; Horace Finmore, 21, Linden Mansions, Highgate, N.; John Griffiths, B.Sc., The Hollies, Upton Park, Chester; James Henry Howgate, B.A., The Avenue, Bakewell, Derbyshire; William Henry Leek, B.A., Elm View, Leigh, Lancashire; Francis Grimshaw Martin, King Henry VIII. School, Coventry; Alfred Mortimer, B.A., Trinity College, Stratford-on-Avon; Sydney Dockeray Stennitt, M.Sc., 16, Richmond Terrace, Whitechurch, Salop; Edmund Henry Stevens, B.A., Haw House, Rothbury, Northumberland; Harold Blythen Stevens, 225, Oxford Street, W.; Francis Henry Wall, 14, Hardman Street, Liverpool.

Of the following papers, those marked * were read:—

*51. "The Kinetics of Chemical Changes which are Reversible. The Decomposition of *as*-Dimethylcarbamide." By CHARLES EDWARD FAWCITT.

This investigation is a continuation of the work already published on carbamide (*Zeit. Phys. Chem.*, 1902, xli., 601) and methylcarbamide (*Trans.*, 1904, lxxxvi., 1581). The theory which was put forward to explain the decomposition of carbamide and methylcarbamide holds good also in the present case.

There is in every respect a very strong similarity between the decomposition of *as*-dimethylcarbamide and that of the cases already studied, and there can be no doubt that all the alkylcarbamides decompose in a similar manner.

Dimethylcarbamide decomposes on heating with acids into the corresponding ammonium salt and dimethylamine salt, the mechanism of the change corresponding with a reaction of the first order having a velocity about six times as great as that of carbamide.

*52. "A New Formation of Acetylcamphor." By MARTIN ONSLOW FORSTER and HILDA MARY JUDD.

The imine, $C_8H_{14} \begin{matrix} \diagup CH \cdot CMe \cdot NH \\ | \\ CO \end{matrix}$, obtained by the

action of magnesium methyl iodide on α -cyanocamphor, crystallises from petroleum and melts at 126°; it has $[\alpha]_D^{26.3} 2^\circ$ in chloroform, and develops an intense blue coloration with alcoholic ferric chloride. It is indifferent towards aqueous alkalis, but is resolved quantitatively by acids into acetylcamphor and ammonia. Magnesium phenyl bromide converts α -cyanocamphor into the corresponding derivative of benzoylcamphor, previously obtained by heating the enolic modification of the diketone with ammonium formate.

The compound, $C_{12}H_{18}O$, produced when magnesium methyl iodide acts on hydroxymethylencamphor or its α -benzoyl derivative, is a pleasant-smelling liquid which boils at 228–229° under 764 m.m., and has $[\alpha]_D^{19.5} 0^\circ$ in chloroform; it is indifferent towards phosphorus pentachloride, phenylcarbimide, hydroxylamine, and ammoniacal silver oxide, but yields camphoric acid with potassium permanganate, which it decolorises immediately. The

di bromide, $C_{12}H_{18}OBr_2$, melts at $152-153^\circ$, and has $[a]_D^{157} 2^\circ$ in chloroform.

The compound, $C_{13}H_{20}O$, prepared from hydroxymethylencamphor and magnesium ethyl iodide, boils at $236-238^\circ$ under 745 m.m., and has $[a]_D^{168} 2^\circ$; its chemical properties resemble those of the lower homologue. The dibromide, $C_{13}H_{20}OBr_2$, melts at 88° , and has $[a]_D^{130} 5^\circ$.

*53. "Preparation and Properties of 1:4:5-Trimethylglyoxaline." By HOOPER ALBERT DICKINSON JOWETT.

In the attempt to prepare substances having a constitution analogous to that of pilocarpine, the following compounds were isolated and characterised:—

4:5-Dimethylglyoxaline, $C_5H_8N_2$, first prepared by Künne (Ber., 1895, xxxviii., 2039), boils at 165° under 10 m.m. pressure, and forms a crystalline nitrate (m. p. 180° , not 164° as stated by Künne) and a *picrate*, yellow needles (m. p. $196-197^\circ$).

1:4:5-Trimethylglyoxaline, $C_6H_{10}N_2$, boils at 117° under 20 m.m. pressure, and crystallises in needles (m. p. 46°); the crystals are soluble in all proportions in water, alcohol, or ether. The nitrate, $C_6H_{10}N_2 \cdot HNO_3 \cdot H_2O$, forms long needles (m. p. 46°); the hydrochloride, $C_6H_{10}N_2 \cdot HCl \cdot H_2O$, forms needles which lose their water of crystallisation over sulphuric acid or at 110° ; the anhydrous salt melts at 199° . The following salts were also prepared:—The *aureichloride*, yellow needles (m. p. 202°); *platinichloride*, yellow crystals (m. p. $224-225^\circ$); *picrate*, yellow needles (m. p. 218°); *methiodide*, long needles (m. p. 158°).

2-Bromo-1:4:5-trimethylglyoxaline, $C_6H_9N_2Br \cdot 2H_2O$, obtained by the bromination of trimethylglyoxaline, crystallises from hot water in long silky needles (m. p. 49°); the anhydrous base melts at 83° . The following salts were also prepared:—*Hydrobromide*, cubical crystals (m. p. 208°); *aureichloride*, yellow needles (m. p. 191°); *picrate*, yellow needles (m. p. 173°).

*54. "Bromomethyl Heptyl Ketone." By HOOPER ALBERT DICKINSON JOWETT.

In the course of some experiments made with the view of preparing the glyoxaline from methyl heptyl ketone, this ketone yielded bromomethyl heptyl ketone by the action of bromine in chloroform solution. By subsequent fractionation of the product, the *bromoketone* was isolated as a pale straw-coloured liquid boiling at 122° under 15 m.m. pressure.

0.1256 gave 0.2228 CO_2 and 0.0928 H_2O . $C = 48.4$; $H = 8.2$. 0.312 „ 0.2652 $AgBr$. $Br = 36.2$. $C_9H_{17}OBr$ requires $C = 48.8$; $H = 7.7$; $Br = 36.2$ per cent.

The liquid has the characteristic odour of the ketone, and acts very quickly on the eyes, causing a copious flow of tears.

Attempts to condense the bromoketone with potassium phthalimide were unsuccessful.

*55. "Limonene Nitrosocyanides and their Derivatives." By FREDERICK PEACOCK LEACH.

It has been previously shown (Trans., 1904, lxxxv., 931) that limonene β -nitrosocyanide gives rise to a crystalline nitrosocyanide (m. p. $90-91^\circ$). The investigation has been continued with the result that both the α - and β -nitrosocyanides of limonene have been found to yield the same isomeric nitrosocyanides, the reaction between the potassium cyanide and the nitrosocyanides being carried out at $25-30^\circ$. The nitrosocyanides are unimolecular and optically active, and therefore analogous to the limonene nitrolamines discovered by Wallach (Annalen, 1889, ccliii., 113).

The α -nitrosocyanide crystallises in prisms (m. p. $90-91^\circ$), whilst the β -compound crystallises in fine woolly needles (m. p. $140-141^\circ$). These isomerides are to be regarded as having the *cis*- and *trans*-configurations, because on hydrolysis, both, by loss of carbon dioxide from their respective acids, give rise to the normal oxime of dihydrocarvone.

From the *d*- and *l*- α -nitrosocyanides were also obtained

the benzoyl derivatives (thin plates, m. p. 108°), methyl and ethyl ethers as viscous oils, and the hydrochloride crystallising from alcohol in thin leaves (m. p. 56°).

The *d*- and *l*-benzoyl derivatives of the β -nitrosocyanide each crystallise from dilute alcohol in long silky needles (m. p. 121°).

The *d*- and *l*- α -amides each gave a methyl ether as a viscous oil, a benzoyl derivative (m. p. 152°), and a hydrochloride (m. p. $100-101^\circ$).

The *d*- and *l*- α -acids each gave ammonium and silver salts, the former being finely crystalline and the latter amorphous. The *d*-methyl ester melts at 65° .

Racemic Compounds.— α -Nitrosocyanide separates in prisms from petroleum (m. p. 81°), its benzoyl derivative melts at 96° . The β -nitrosocyanide forms fine needles (m. p. $159-160^\circ$) and its benzoyl derivative crystallises in needles melting at 98° .

*56. "The Action of Carbon Monoxide on Ammonia." By HERBERT JACKSON and DUDLEY NORTHALL-LAURIE.

The authors have studied the behaviour of these gases when heated together in the presence of platinum, or when subjected to electric sparks or high frequency discharges. They find that the main reaction is the formation of ammonium cyanate, which, under the conditions of the experiment, rapidly changes to carbamide. Hydrogen is produced, and some of this interacts to give water, which in its turn brings about the formation of ammonium carbonate. The amount of ammonium cyanide formed is small. Other products are obtained by prolonging the experiment, but only in quantities which are small compared with the yield of the main product, carbamide.

DISCUSSION.

Prof. E. J. MILLS said the authors' experiments reminded him of some of his own carried out a number of years ago. He then found that, by passing a current of mixed carbonic oxide and ammonia gas over strongly heated caustic potash in presence of carbon, cyanide was formed in large quantity. In fact, a potassium salt containing more than 70 per cent of cyanide was readily produced. The carbon, of course, precluded the formation of any cyanate.

*57. "The Action of Acetylene on Aqueous and Hydrochloric Acid Solutions of Mercuric Chloride." By JOHN SAMUEL STRAFFORD BRAKE.

Bilz and Mumm (Ber., 1905, xxxvii., 4417) and Hofmann (Ber., 1904, xxxvii., 4459) show that the white precipitate obtained when acetylene is passed into aqueous mercuric chloride is trichloromercuriacetaldehyde, $C(HgCl)_3 \cdot CHO$. The author obtained results three years ago which agree closely with those of the above and other observers, but attention is now called to the considerable differences between the determined and calculated values, the analytical results for mercury being very low, whilst those for chlorine are too high. From the reactions, however, the foregoing constitution seems to be the most reasonable one.

Berge and Reychler (Bull. Soc. Chim., 1897, xvii., 218) state that acetylene has no action on dilute hydrochloric acid solutions of mercuric chloride, but the author obtained a fine crystalline substance, which was afterwards found to have been described by Biginelli (Ann. Farm. Chim., 1898, xvi.), who ascribed to it the constitution $Cl \cdot HC \cdot CH \cdot HgCl$ from estimations of mercury and chlorine only. This conclusion has been confirmed by complete analysis, and the compound is further described.

Biginelli states that when boiled with water the above compound yields $CH_2 \cdot CH \cdot HgCl$, but the author fails to obtain such a result. It is shown that the product is really trichloromercuriacetaldehyde, but a certain amount of mercurous chloride is also present, this being ascribed to the reducing action of the aldehyde liberated on the mercuric chloride.

Biginelli's statement that $C_2H_2 \cdot HgCl_2$ gives with alkalis an acetylde, $(C_2H_2)_2HgO$, cannot be confirmed, but

evidence from analyses and properties shows the substance to be identical with the acetylide $3C_2H_2, H_2O$ described by Travers and Plimpton (*Trans.*, 1894, lxx., 264). Attempts are being made to prepare the anhydrous acetylide.

The first action of acetylene with mercuric chloride appears, therefore, to be one of simple combination, the additive product being then decomposed by water with the production of aldehyde and $C(HgCl)_3 \cdot CHO$.

58. "The Basic Properties of Oxygen at Low Temperatures. Additive Compounds of the Halogens with Organic Substances containing Oxygen." By DOUGLAS MCINTOSH.

Crystalline compounds of chlorine with methyl and ethyl alcohols have been obtained at low temperatures (-80°), the formula of the former being probably CH_3OCl , whilst the latter has the composition C_2H_5OCl ; their melting-points are -96° and -88° respectively. Compounds of a similar type were isolated containing bromine, the methyl alcohol derivative, CH_3OBr , being a red crystalline substance melting at -53° .

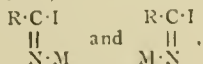
Methyl ether, although not yielding a solid product with chlorine at -95° , furnished a bromine compound, C_2H_5OBr , melting at -68° . Ethyl ether yielded $C_4H_{10}OCl_2$ (m. p. -51°) and $C_4H_{10}OBr_2$ (m. p. -40°).

Acetone combined with chlorine to form $C_3H_6OCl_2$ (m. p. -53°), whilst with bromine it gave rise to $C_3H_6OBr_2$ (m. p. 12°).

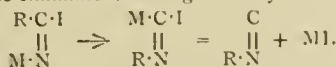
Ethyl acetate yielded the additive products $CH_3 \cdot CO_2Et \cdot Cl_3$ (m. p. -64°) and $CH_3 \cdot CO_2Et \cdot Br_3$ (m. p. -39°). Acetaldehyde and acetic acid also seem capable of combining additively with chlorine and bromine at low temperatures.

59. "Note on the Interaction of Metallic Cyanides and Organic Halides." By NEVIL VINCENT SIDGWICK.

It is possible to explain the formation of both nitriles and isocyanides in this reaction by means of the same additive compound, and that of the most probable type, in which the addition has been to the bivalent carbon only. Such a compound, like an unsymmetrical oxime, could exist in two stereoisomeric forms,—



where $M = K, Ag, \&c.$, and $R = \text{alkyl or acyl}$. The first of these would easily lose MI to give a nitrile, in accordance with Nef's view, but the second could not, as the metal and the halogen are too far apart, and it would therefore undergo the Beckmann reaction. This change brings these substituents nearer together, so that now they combine and become eliminated, leaving an isocyanide:—



If this is the case, we must suppose that an alkyl iodide and potassium cyanide, or an acyl halide and silver cyanide (which yield nitriles), give the "syn-haloid form, and an alkyl iodide and silver cyanide the "anti-haloid."

It may also be pointed out that neither of the formulæ of hydrocyanic acid can be that of a strong acid, because if it were the alkali salts would be derived from that form, and would not be, as they are, highly hydrolysed in solution.

60. "The Chemical Dynamics of the Reactions between Sodium Thiosulphate and Organic Halogen Compounds. Part II. Halogen Substituted Acetates." By ARTHUR SLATOR.

Many of the halogen substituted acetates interact more readily with sodium thiosulphate than the corresponding methyl haloids. The reactions with ethyl iodoacetate and methyl, ethyl, and sodium bromo- and chloro-acetates have been investigated, and shown in all cases to be bimolecular reactions. The esters are considerably more reactive than the sodium salts. The temperature quotient of the reactions with the esters was found to be in all five

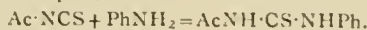
cases approximately 2.8; with the sodium salts, an appreciably smaller value was obtained. The reaction between ethyl bromoacetate and potassium, ammonium, barium, strontium, sodium silver, lead, and sodium lead thiosulphates have been measured, and from the results obtained it is probable that the reaction is primarily connected with the $S_2O_3^{--}$ ion, and that the undissociated or partially dissociated salts are relatively inactive. The velocity of reaction is proportional to the concentration of the $S_2O_3^{--}$ ion, and the measurements may therefore be used to estimate such concentrations. The dissociation constant of lead thiosulphate measured in this way was found to have the value $[Pb^{++}][S_2O_3^{--}]/[PbS_2O_3] = 1.5 \times 10^{-4}$.

61. "The Tautomerism of Acetyl Thiocyanate." By AUGUSTUS EDWARD DIXON and JOHN HAWTHORNE.

When acetyl thiocyanate is brought into contact with aniline at temperatures ranging from -12° to about 120° , in presence of an inert solvent, such as benzene, interaction occurs spontaneously, with development of much heat, the chemical changes running concurrently on two distinct lines:—(1) A change by double decomposition, in which the sulphur appears wholly in the form of thiocyanic acid as shown by the equation—



(2) an additive process in which the sulphur plays a thiocarbimide part, thus:—



At 87° , one-half of the total weight of product consists of acetanilide together with aniline thiocyanate, the remainder being acetylphenylthiocarbamide; at lower temperatures, the proportion of thiocyanate and anilide rises, and for temperatures below 30° reaches 90 per cent and upwards of the total, whilst at temperatures above 87° the proportions are reversed, the yield of thiocarbamide increasing, with a corresponding decrease in the amount of the other two products, until in the neighbourhood of 120° the sum of the latter diminishes to some 2 or 3 per cent.

Although the thiocarbimide character of acetyl thiocyanate, as measured by its power to yield the additive compound, acetylphenylthiocarbamide, increases regularly with the temperature of interaction, it would seem that this power is not acquired through ordinary isomeric change. For in all cases hitherto observed, the transformation by heat of a thiocyanate into a thiocarbimide is non-reversible, the latter representing the stable and permanent form, whereas here the percentage of acetylphenylthiocarbamide resulting at any given temperature is not affected by previous heating of the thiocyanate, but is determined solely by its temperature at the moment of interaction.

These phenomena come neither under the head of tautomerism proper, which is conditioned through the intramolecular migration of a hydrogen atom, nor into the category of migration of whole atomic groups; in point of elasticity, they present some resemblance to dissociation changes, but until further inquiry has been made the authors prefer not to advance definite views as to their nature and causation.

62. "A Method of Determining the Specific Gravity of Soluble Salts by Displacement in their Own Mother-liquor, and its Application in the Case of the Alkali Halides." By JOHN YOUNG BUCHANAN.

The method presents obvious difficulties of manipulation, but as it furnishes at one and the same time the specific gravity of the salt and that of its mother-liquor, both being determined at the temperature of equilibrium, it may be sometimes advisable to encounter these difficulties.

This method has been applied in the case of the chlorides, bromides, and iodides of potassium, rubidium, and cesium, and the following are the values obtained for the specific gravity D of each of these salts at the temperature T , referred to that of distilled water at the same temperature as unity.

Salt, MR.	Temperature, T.	Specific gravity, D.
KCl	23.4°	1.951
KBr	23.4°	2.679
KI	24.3°	3.043
RbCl	22.9°	2.706
RbBr	23.0°	3.210
RbI	24.3°	3.428
CsCl	23.1°	3.982
CsBr	21.4°	4.455
CsI	22.8°	4.508

63. "The Combination of Mercaptans with Unsaturated Ketonic Compounds." By SIEGFRIED RUHEMANN.

The author has continued his research (*Trans.*, 1905, lxxxvii., 17) on the union of mercaptans with olefinic ketonic compounds effected under the influence of bases, since on using hydrogen chloride as catalytic agent. Posner frequently obtained mixtures, owing to the fact that mercaptans, besides combining additively at the ethylene linking, partly condensed with the ketonic group. Besides the compounds which previously had been described as being formed from mercaptans and mono-olefinic ketones,

$C:C:CO-$, other substances have been prepared by the union of benzylideneacetophenone and ethyl benzylidenebenzoylacetate.

Cinnamylideneacetophenone, the di-olefinic ketone of the type $C:CH:CH:CH:CO-$, as shown before (*loc. cit.*),

takes up 1 mol. only of either phenyl mercaptan or isoamyl mercaptan, instead of 2 mols., as stated by Posner (*Ber.*, 1904, xxxvii., 509). This investigator has since acknowledged the error. The behaviour of cinnamylideneacetone is analogous; this substance unites with 1 mol. of phenyl mercaptan to yield the compound $C_6H_5:CH:CH:CH(S:C_6H_5):CH_2:CO:CH_3$ (m. p. 53–54°), whilst according to Posner's statement an oil is thus formed, which on oxidation is transformed into a disulphone.

In harmony with the author's result is the fact that cinnamylidenebenzylideneacetone,—



unites with 1 mol. of either isoamyl mercaptan or phenyl mercaptan, but 2 mols. of mercaptan may also be added to the tri-olefinic ketone, yet the separation of the compound from the additive product with 1 mol. of the mercaptan which is formed at the same time has not been effected.

Moreover, the acetylenic ketone, methoxybenzoylphenylacetylene, $C_6H_5:C:C:CO:C_6H_4:O:CH_3$, unites with 1 mol. of phenyl mercaptan to form—



(m. p. 121–122°), which is yellow as compared with the additive substances of mercaptans with olefinic ketones, which are almost all colourless.

The olefinic cyclic ketones, benzylidenephénylmethylpyrazolone, $C_6H_5:N \begin{matrix} \diagup N-C:CH_3 \\ \diagdown CO:C:CH:C_6H_5 \end{matrix}$, and benzylidene-

phenylazlactone, $C_6H_5:C \begin{matrix} \diagup N:C:CH:C_6H_5 \\ \diagdown O:CO \end{matrix}$, unite with

phenyl mercaptan, but, whilst the pyrazolone derivative forms an additive product (m. p. 140°) with 1 mol. of the mercaptan, the azlactone takes up 2 mols. of phenyl mercaptan to yield a compound (m. p. 156–157°) which probably has the formula—



64. "The Existence of a Carbide of Magnesium." By J. TRENGOVE NANCE.

The residue left after burning magnesium in carbon dioxide, if shaken with water or dilute hydrochloric acid, gives a smell resembling that of geraniums. This smell is always obtained when magnesium is heated with carbon,

or in air containing carbon dioxide, and the residue treated as above. It is due to the presence of a hydrocarbon formed by the action of water on the residue, for it is driven off by heat, can be concentrated in a distillate, and if the gas is passed through a red-hot tube together with air, carbon dioxide is formed.

The presence of acetylene from a carbide of magnesium being suspected, a mixture of magnesium powder and powdered wood charcoal was gently ignited. The yellowish residue was treated with dilute hydrochloric acid, and the gas, mainly hydrogen, which was vigorously evolved, gave the following indications of the presence of acetylene. It burnt with a faintly luminous, two-zoned flame, and when passed through ammoniacal cuprous chloride it produced a brownish-red precipitate. With ammoniacal cupric solutions, decolorised by hydroxylamine, a brilliant crimson precipitate was obtained (compare Illosvay von Nagy Illosva, *Ber.*, 1899, xxxii., 2697; *Abstr.*, 1900, ii., 52). These precipitates dissolved, wholly or partially, in dilute hydrochloric acid, with evolution of acetylene, copper passing into solution.

By analogy, the carbide formed should be MgC_2 , but it was not obtained in a sufficiently pure condition for a quantitative analysis. It does not seem to interact as vigorously with water as the calcium compound.

65. "Isomeric Salts of the Type $NR_1R_2H_3$. (A correction). Isomeric Forms of *d*-Bromo- and *d*-Chloro-camphorsulphonic Acids." By FREDERIC STANLEY KIPPING.

The further study of the isomeric α - and β -salts, which the author obtained by combining ordinary *d*-bromo- and *d*-chloro-camphorsulphonic acids with *dl*- and with optically active bases, such as hydrindamine (*Trans.*, 1900, lxxvii., 861; 1903, lxxxiii., 873), benzylhydrindamine (Kipping and Hall, *Trans.*, 1901, lxxix., 430), methylhydrindamine (Tattersall and Kipping, *Trans.*, 1903, lxxxiii., 918), and *l*-menthylamine (Tutin and Kipping, *Trans.*, 1904, lxxxv., 65), has brought to light the fact that the isomerism of these compounds is not determined by a difference in the arrangement in space of the groups united with the quinquivalent nitrogen atom, such as is represented by the symbols $N \begin{matrix} \diagup H \\ \diagdown N \end{matrix}$ and $H \begin{matrix} \diagup N \\ \diagdown N \end{matrix}$, but to

the existence of *cis*- and *trans*-forms of *d*-bromo- and *d*-chloro-camphorsulphonic acids, containing the groups $N \begin{matrix} \diagup C-H \\ \diagdown C-X \end{matrix}$ and $H \begin{matrix} \diagup C-X \\ \diagdown C-H \end{matrix}$, and now distinguished as the

α - or normal and β - or *iso*-acids.

The isomeric acids are stable in neutral solutions of their salts in the free state and in presence of mineral acids, even at 100°; in presence of a free base, however, such as caustic potash, baryta (sodium carbonate), hydrindamine, &c., the salts of the normal acid are transformed to a small extent into those of the *iso*-form, whereas the latter are almost entirely converted into salts of the normal acid, equilibrium being attained apparently when at least 90–95 per cent of the compound exists in the normal form. During this change, the two modifications doubtless become identical, both passing through one and the same unstable enolic form.

All the salts of ordinary *d*-bromocamphorsulphonic acid which have hitherto been described by the author and by others, excepting those obtained from *d*- and *l*-hydrindamine, and then separated from the β -forms, are probably mixtures of the two isomerides; the only salts of the *iso*-acids which are yet known are those previously described as *dl*-hydrindamine *d*-bromocamphorsulphonate and the β -modifications of *d*- and *l*-hydrindamine chlorocamphorsulphonates.

The molecular rotation of *iso-d*-bromocamphorsulphonic acid is approximately $[M]_D + 177^\circ$, that of the corresponding chloro acid being about $[M]_D + 233^\circ$, so that in one case the normal, in the other the *iso*-acid, has much the higher value.

No new facts have yet been obtained as to the cause of the formation of the isomeric salts of *cis*- π -camphanic acid, but in view of the above-mentioned results it would seem that the explanation previously suggested is not the true one.

66. "Isomerism of α -Bromo- and α -Chloro-camphor." By FREDERIC STANLEY KIPPING.

The fact that the sulphonic acids derived from α -bromo- and α -chloro-camphor may be transformed into isomerides by the action of bases rendered it extremely probable that the simple halogen derivatives themselves would give rise to isomerides under similar conditions; the following experiments show this to be the case.

Pure ordinary α -bromocamphor, dissolved in 96 per cent alcohol, gave $[\alpha]_D^{25} +135$; on adding a very small quantity of sodium ethoxide to the solution, the specific rotation fell to $[\alpha]_D^{25} +122$, a value which did not change appreciably during twenty-four hours, or on acidifying the solution with acetic acid. Ordinary bromocamphor, therefore, is partially converted into the *iso*-form, which has a lower specific rotation, and in the alkaline solution a condition of equilibrium between the isomerides is rapidly attained.

Judging from the behaviour of bromocamphorsulphonic acid, this *iso*- α -bromocamphor should be stable in acid solution. Accordingly some ordinary bromocamphor was treated in alcoholic solution with sodium ethoxide and the solution almost immediately acidified; on evaporating, crystals of ordinary bromocamphor were first deposited; these were separated from the mother-liquor, and treated again with sodium ethoxide and acid successively, these operations being repeated several times. The combined mother-liquors gave on evaporation an oily deposit which was distilled in steam, and then fractionally crystallised from light petroleum; the first deposits consisted of ordinary bromocamphor, but the later fractions crystallised slowly in camphor-like masses. The specific rotation of this product, which no doubt still contained ordinary bromocamphor, was $[\alpha]_D^{25} +38.5$ in 96 per cent alcohol; when, however, a trace of sodium ethoxide was added to the alcoholic solution, the specific rotation increased rapidly, and attained a constant value approximately the same as that of the solution of ordinary bromocamphor to which sodium ethoxide had been added.

When, moreover, the camphor-like mass was dissolved in a little alcohol and a few drops of caustic soda added, a large quantity of ordinary bromocamphor separated in crystals.

These experiments seem to establish the existence of normal and *iso*-forms of α -bromocamphor, and they explain the use of the caustic potash or caustic soda which is added in isolating ordinary bromocamphor from the crude product of the bromination of camphor; this crude product, as shown by Marsh (*Trans.*, 1890, lvii., 828), doubtless consists of a mixture of the two isomerides, possibly together with unchanged camphor, but the isolation of the pure *iso*-form would most likely be a very hard task, which, as Marsh himself suggests, he probably did not accomplish. Similar experiments to the above indicate that ordinary α -chloro-camphor is also capable of existence in a stable *iso*-form, and the matter is being further investigated.

67. "1-Phenylethylamine." By FREDERIC STANLEY KIPPING and ALBERT EDWARD HUNTER.

In No. 3 of the current *Berichte* (xxxviii., 801) there appears a paper by Marckwald and Meth, "Über Amidbildung Zwischen Optisch-activen Säuren und Basen und die Optisch-activen α -Amidoethylbenzolen," containing certain statements respecting some work of ours to which we take exception (*Trans.*, 1903, lxxxiii., 1147). Firstly, "Ihnen gelang wohl die Reindarstellung des Salzes der *l*-Base, aber die gewonnene Menge reichte zur Isolirung der reinen Base nicht aus"; also "K. and H. haben aus Mangel an Material das Drehungsvermögen des von ihnen gewonnenen, *l*-Phenyläthylamin nur in wässrig alkoholischer Lösung bestimmt."

Neither statement is correct; we did not prepare the

anhydrous base or determine its specific rotation merely because we were solely engaged in studying its salts.

The statement "Dennach haben Kipping and Hunter annähernd reines *l*-Phenyläthylamin in Händen gehabt" suggests that our base contained some of the *d*-isomeride; this was not the case, and the specific rotation (-3.7) of the hydrochloride prepared by us was in fact slightly higher than that (-3.5) of Marckwald and Meth's preparation, although the difference is within the limits of experimental error.

The fact that the benzoyl derivative of the *l*-base melts at the same temperature as that of the *dl*-base, when both are crystallised from alcohol, and the fact that the specific rotation of the *l*-benzoyl derivative is extremely small according to Marckwald and Meth (only $+0.3$ in alcoholic solution) led us to state that the base "seems" to undergo racemisation during the preparation of its benzoyl derivative; our statement that "mixtures of the three compounds also melted at 120° " (*loc. cit.*, p. 1148) is doubtless correct, as the mixtures consisted of approximately equal quantities of the *d*-, *l*-, and *dl*-benzoyl derivatives, and we omitted to examine the behaviour of a mixture of the *l*- and *dl*-compounds only.

68. "The Influence of the Hydroxyl and Alkoxy Groups on the Velocity of Saponification." Part I. By ALEXANDER FINDLAY and WILLIAM ERNEST STEPHEN TURNER.

The following values of the saponification constant in aqueous solution have been determined (at 25°).

Ester.	k.
Ethyl phenylacetate	12.4
Methyl mandelate	157
Ethyl mandelate	66
Propyl mandelate	55
Ethyl phenylmethoxyacetate	23.3
Ethyl phenylethoxyacetate	15.7
Ethyl phenylpropoxyacetate	(13.3)

The value for ethyl phenylpropoxyacetate was calculated from the values obtained in alcoholic solution.

The numbers in the foregoing table show at once the greatly accelerating influence which the hydroxyl group exercises on the velocity of saponification, the constant being increased to about five times (for example, ethyl phenylacetate and ethyl mandelate). The increase in the affinity constants of the corresponding acids is about eight times. On replacing the hydrogen of the hydroxyl by an alkyl group, the velocity of saponification is diminished, and the diminution increases regularly with the mass of the alkyl group.

The velocity of saponification was also studied in aqueous alcoholic solution, the strength of which was 30 and 60 per cent by weight. The values obtained were, of course, diminished by the addition of alcohol; they are contained in the following table:—

Ester.	In 30 per cent alcohol. k.	In 60 per cent alcohol. k.
Ethyl phenylacetate	8.6	(6)
Methyl mandelate	(109)	(84)
Ethyl mandelate	49.4	29.1
Propyl mandelate	39.5	22.7
Ethyl phenylmethoxyacetate	15.2	(8)
Ethyl phenylethoxyacetate	10.2	(6)
Ethyl phenylpropoxyacetate	—	(5)

The numbers enclosed in brackets are only approximate, as in the case of the esters to which they apply there was a great decrease in the value of the "constant" with the time.

PHYSICAL SOCIETY.

Ordinary Meeting, April 14th, 1905.

Dr. R. T. GLAZERBROOK, F.R.S., Past-President, in the Chair.

Mr. R. J. SOWTER read a paper on "Ellipsoidal Lenses."

The paper extends the treatment of thin ellipsoidal or astigmatic lenses, and gives a simple solution for complex

problems of the following types:—"To determine the astigmatic pencil, after refraction of an astigmatic pencil by an ellipsoidal lens." And "to find the ellipsoidal lens equivalent to two cylindrical lenses placed a definite distance apart, with their axes inclined at an angle." The method of treatment can be applied to crossed ellipsoidal lenses, in contact or separated, and is applicable in general to astigmatic pencils.

It has been shown by Prof. S. P. Thompson and the author that, for obliquely-crossed cylindrical lenses, an important double-angled parallelogram of powers can be constructed. This parallelogram is associated with the resolution of a lens-power, P , into the two powers $P \cos^2 \theta$, $P \sin^2 \theta$ at right-angles. If an astigmatic pencil having two focal lines at distances u and v from an ellipsoidal lens of focal powers A and B is refracted by the lens, which is further defined in position with respect to the focal lines by θ , then, by resolving along two directions at right-angles and adopting the curvature notation we get $-(U \cos^2 \theta + V \sin^2 \theta) + U' \cos^2 \theta' + V' \sin^2 \theta' = A$ and $-(U \sin^2 \theta + V \cos^2 \theta) + U' \sin^2 \theta' + V' \cos^2 \theta' = B$; where $U = 1/u$ and $V = 1/v$, and U' , V' , θ' define the focal lines in the refracted pencil. The above equations give $-(U + V) + U' + V' = A + B$ and $-(U - V) \cos 2\theta + (U' - V') \cos 2\theta' = A - B$. This last equation shows that the power parallelogram has its sides equal to $(U - V)$, $(A - B)$, its angle 2θ , the diagonal $(U' - V')$, and the inclination of the diagonal $2\theta'$. The parallelogram affords the equation $(U' - V')(U - V) = \sin 2\theta / \sin 2\theta'$. This equation, together with the two preceding ones, gives a complete solution. The usual lengthy solution by the use of the characteristic function resolves itself into that given by Herman employing Malus's theorem. If a parallel pencil falls upon the first lens of a crossed and separated cylindrical combination, we have the equations $-U \cos^2 \theta + V' \cos^2 \theta' + V' \sin^2 \theta' = A$, $-U \sin^2 \theta + U' \sin^2 \theta' + V' \cos^2 \theta' = 0$; where U is the equatorial curvature of the cylindrical wave at the second lens (power A), θ is the angle of crossing of the lenses, and U' , V' , θ' define the refracted pencil, and consequently the equivalent ellipsoidal lens. Two experiments are described which gave results in agreement with those deduced from the equations.

Mr. W. BENNETT congratulated the author on his interesting solution of an important problem. The method of resolving the convergence or divergence of the incident pencil, and the power of the lens, in two directions at right angles should prove of great utility, particularly in arithmetical computation. Referring to the statements at the end of the paper, he asked if it was not a fact that any surface could be regarded as paraboloidal in the neighbourhood of a point. If we consider the paraboloid of curvature to be adjusted to the surface at the point, and neglect quantities of the first order, the normals of a small element of the paraboloid pass through two lines, the difference between the element of the surface and the element of the paraboloid depending only on quantities of the second order. The matter may be looked at in another way; the normals to any wave-front touch a caustic surface of two sheets, the normals to any finite region of the wave-front mapping out a finite region on each sheet of the caustic. As the element of the wave-front is made small the corresponding elements of the caustic become smaller, but do not in general become linear. Their projections, however, on the orthogonal surface become approximately linear, and hence the normals pass approximately through two straight lines, and any thin pencil may be regarded as a standard astigmatic pencil. The standard astigmatic pencil of finite aperture, however, cannot exist. Maxwell has shown that the only form of wave-front for which the two sheets of the caustic surface degenerate into lines is the cyclide of Bonnet. These focal lines are not straight, but are two conics in planes at right angles to one another, the foci of either conic lying on the vertices of the other. In the general case these conics are an ellipse and a

hyperbola respectively. In one particular case the conics are parabolas and in another they become a circle and a straight line through the centre of the circle. The wave-front in the latter case is an anchor-ring.

A paper on "*The Determination of the Moment of Inertia of the Magnets used in the Measurement of the Horizontal Component of the Earth's Field*" was read by Dr. W. WATSON.

One of the constants required when determining the horizontal component of the earth's magnetic field by the ordinary method is the moment of inertia of the magnet which is used in the vibration experiment. It is usual to determine the moment of inertia of the cylindrical brass bar supplied with each instrument by calculation, then by measuring the period of the magnet alone, and when loaded with this bar to calculate the moment of inertia of the magnet. This method presupposes that the density of the inertia-bar is uniform throughout. It is easy to secure a bar of which the density is uniform throughout, and further it is difficult to test whether such uniformity has been secured. The author thinks that more reliable and uniform results would be obtained by determining once for all, with very great care, the moment of inertia of a standard bar and then determining the moment of inertia of the bars supplied with the different magnetometers, by comparing them with the standard bar experimentally. In the paper is described an instrument suitable for comparing the moment of inertia of bars, together with some experiments made with a view to determining the moment of inertia of a standard bar, and an investigation of the influence of the air upon the period. The bars which have been compared are as follows:—(1) rolled brass; (2) cast silver; (3) rolled copper; (4) copper with 5 per cent zinc; (5) copper with 5 per cent phosphide of tin; (6) gun-metal; (7, 8, 9) rolled copper; and (10) a rolled brass bar with slightly rounded ends and gilt. The periods of oscillation of the bars when resting in a cradle hung by a quartz fibre were determined accurately with the instrument described. Owing to the fact that the rigidity of fused silica increases as the temperature rises, the period changes very little with temperature and the corrections for changes in temperature can be made without difficulty. With an initial amplitude less than 5° the period is not, within the limits of accuracy of the observations, affected by the variation in amplitude. Variations in period due to the variation of the rigidity of the fibre with the load upon it were found to be negligible. In order to test the influence on the period of the air carried by the bars when swinging, a vacuum chamber was used which enclosed the whole instrument. The procedure adopted was to observe the period at atmospheric pressure, then exhaust and observe the period, and finally the air having been readmitted to observe again at atmospheric pressure. The results showed an increase of moment of inertia for 76 cms. increase in pressure of the order 0.1 per cent. The author has investigated the effect of the air in the case of the magnets used in the Kew pattern unifilar magnetometer, and finds that it may cause an error of about 4.4%. The paper concludes with a comparison of Dr. Watson's bars with some belonging to the National Physical Laboratory.

Dr. C. CHREE expressed his interest in the paper, and remarked that the want of homogeneity in inertia bars was a source of serious trouble in magnetometer work. The variation in density might be as much as 5 or even 10 per cent. He favoured the adoption of a standard bar which could be swung in various magnetometers. He expressed his interest in the size of the error which may affect the value of the horizontal force due to the increased moment of inertia caused by the air. A similar error entered into pendulum observations. With regard to the rigidity of quartz fibres, he was inclined to think that there would be a change in rigidity with a change in load.

Mr. W. A. PRICE asked if the difference in magnetic permeability between air and the material of the bars was sufficient to affect the period, and also if there were any

other fibres whose rigidity increased with rise of temperature.

The CHAIRMAN expressed his interest in the paper and said that he had followed the course of the work. In attempting to get an accurate value for H it was most important to check the homogeneity of the inertia bar. The value of the moment of inertia should be known with great accuracy. Four or five years ago he suggested experiments similar to those described by Dr. Watson for measuring inertia bars, and although preliminary observations were made they were not carried far.

Dr. WATSON said he knew of no other substance but quartz which was suitable for the experiments he had performed. He had not found any variation of period due to magnetic permeability. With regard to Dr. Glazebrook's remarks, he said the measurement of the diameter of the bars was easy, but that the determination of the length was much more difficult.

Dr. W. WATSON gave an Exhibition of a Series of Lecture Experiments illustrating the Properties of the Gaseous Ions produced by Radium and other Sources.

Many well-known experiments on the subject were shown by Dr. Watson, who pointed out the precautions which must be observed in order to ensure success at lecture demonstrations.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxi., No. 13, March 27, 1905.

Monochlor-derivatives of Methylcyclohexanone.—Paul Sabatier and Alp. Mailhe.—The formula assigned to methylcyclohexane, $\text{CH}_3\text{—CH} < \begin{smallmatrix} \text{CH}_2\text{—CH}_2 \\ \text{CH}_2\text{—CH}_2 \end{smallmatrix} > \text{CH}_2$, shows the possible existence of five monochlor-derivatives of different formulae, the chlorine being substituted either in the radicle CH_3 , giving the primary chloro-derivative; in CH , forming the tertiary chloro-derivatives; or in the terms CH_2 (2, 3, or 4), giving ortho, meta, or para secondary chloro-derivatives. These five compounds are the hydrochloric ethers of the five corresponding alcohols derived from methylcyclohexane. The authors prepare these five ethers by the action of phosphorus perchloride in the cold on each of the alcohols. The formation always takes place with the separation of a certain amount of naphthenic carbide, C_7H_{12} .

Oxidation of Metals at Ordinary Temperatures in presence of Ammonia.—C. Matignon and C. Desplantes.—The presence of ammonia renders slow oxidation of certain metals possible at ordinary temperatures. Such metals are mercury, silver, nickel, cobalt, molybdenum, and tungsten; these forming oxides soluble in ammonia. This property has been known for a long time in the case of copper.

Cryoscopic Experiments in Hydrocyanic Acid.—M. Lespieau.—Investigations on trichloroacetic and sulphuric acids show that these two acids, although strongly electrolytically dissociated in aqueous solution, are not perceptibly dissociated in hydrocyanic solutions of the same concentration. This fact is in perfect agreement with Kahlenberg's observations, who showed that such solutions were bad conductors. On the contrary, hydrocyanic solutions of potassium salts are better conductors than aqueous solutions of the same concentration. The author finds in all cases that, on distillation, almost the whole of the hydrocyanic acid can be recovered in a state of purity.

Ferric Ethylate.—Paul Nicolardot.—The author makes a series of experiments on the preparation of ferric ethylate, and finds that soluble ferric ethylate does not exist any more than soluble ferric hydrate.

Substitution Products of Natural Lævo-leucine.—MM. Hugounenq and Morel.—The carbimide of ethylic ether of leucine, $\text{CO.NCH} < \begin{smallmatrix} \text{CH}_2\text{—CH} < \text{CH}^3 \\ \text{CO—OC}_2\text{H}_5 \end{smallmatrix} > \text{CH}^3$, can be used

for the preparation of a number of substitution products, such as leucine-hydantoic acid, mixed urea of leucine and aniline, and also symmetric urea of leucine.

Pyridine Iodomercurates.—Maurice François.—The author prepares four iodomercurates of pyridine by the action of a solution of pyridine iodohydrate on mercuric iodide. They are formed by mixing a solution of pyridine chlorohydrate containing an excess of hydrochloric acid with a solution of mercuric iodide in potassium iodide. All the iodomercurates undergo a limited decomposition under the action of water—an insoluble mercuric iodide being produced and pyridine iodohydrate being left in solution. The action is the same as that of ammonium iodomercurate. This decomposition is, however, more marked than in the case of substances containing more mercuric iodide.

Heat of Formation of Calcium Hydride and Nitride.—A. Guntz and Henry Basset, jun.—Calcium hydride prepared by heating calcium in a current of hydrogen is used for finding the heat of formation of this substance. To make the determination the hydride and the metal calcium are dissolved in a dilute solution of hydrochloric acid. The authors' results are:— $\text{Ca sol.} + n\text{HCl dil.} = \text{CaCl}_2 \text{ diss.} + \text{H}_2 \text{ dry} + 129 \text{ cal.}$, $\text{CaH}_2 \text{ sol.} + n\text{HCl dil.} = \text{CaCl}_2 \text{ diss.} + 2\text{H}_2 \text{ dry} + 82.8 \text{ cal.}$ The heat of formation of the nitride is found in the same manner, allowance being made for the small quantity of metal which it contains, and which it is impossible to eliminate. The experiment gives $\text{Ca}_3\text{N}_2 + n\text{HCl dil.} = 3\text{CaCl}_2 \text{ diss.} + 2\text{NH}_4\text{Cl diss.} + 342.7 \text{ cal.}$ By calculation, $\text{Ca sol.} + \text{H}_2 \text{ gaseous} = \text{CaH}_2 \text{ sol.} + 46.2 \text{ cal.}$ and $3\text{Ca sol.} + \text{N}_2 \text{ gaseous} = \text{Ca}_3\text{N}_2 \text{ sol.} + 112.2 \text{ cal.}$

Applications of Watts' Principle to the Dissociation of Carbonates of Lead and Silver.—Albert Colson.—Theoretically and practically the decomposition of lead carbonate in the same manner as silver carbonate is reversible when the polymerisation produced by temperature is eliminated. This conclusion also extends most probably to other metallic carbonates. A complete absence of water not only prevents the re-constitution of silver and lead carbonates, but retards their decomposition to such an extent that an equilibrium obtained in six or seven hours in a damp atmosphere takes ten or twelve times as long to be reached when the decomposition of the carbonate takes place under identical temperature conditions, but where every trace of water is absorbed by P_2O_5 . This is probably a general principle.

Heat of Formation of Oximes.—Ph. Landrieu.—Already noticed.

Royal Institution.—On Tuesday next, May 2, at 5 o'clock, Prof. L. C. Miall delivers the first of three on the "Study of Extinct Animals"; and on Thursday, May 4, at the same hour, Prof. Sir James Dewar commences a course of three lectures on "Flame"; and on Saturday, May 6, at 3 o'clock, Prof. Marshall Ward begins a course of two lectures on "Moulds and Mouldiness." The Friday Evening Discourse on May 5 will be delivered by Prof. H. E. Armstrong, the subject being "Problems Underlying Nutrition," on May 12 by Prof. W. Fox. Nicholls on "The Pressure due to Radiation," and on May 19 by Sir Charles Eliot on "The Native Races of the British East Africa Protectorate."

MEETINGS FOR THE WEEK.

- MONDAY, May 1st.—Royal Institution, 5. Annual Meeting.
Society of Chemical Industry, 8. "Study of the Action of Hydrogen Peroxide on a Photographic Plate in the Dark" and "Influence of the Length of the Time of Development on the Degree of Darkening of the Photographic Plate," by Prof. C. Otsuki.
- TUESDAY, 2nd.—Royal Institution, 5. "The Study of Extinct Animals," by Prof. L. C. Miall, F.R.S., &c.
Society of Arts, 4.30. "The Monumental Treatment of Bronze," by J. Starkie Gardner, P.S.A.
- WEDNESDAY, 3rd.—Society of Arts, 8. "Recent Excavations in Rome," by Mrs. Burton-Brown.
- THURSDAY, 4th.—Royal Institution, 5. "Flame," by Prof. Sir James Dewar, F.R.S., &c.
Chemical, 8. "Synthesis of Substances Allied to Adrenaline," by H. D. Dakin. "Methylation of *p*-Aminobenzoic Acid by means of Methyl Sulphate," by J. Johnston. "Notes on Sodium Alum," by J. M. Wadmore. "Camphor- ψ -semicarbazide," by M. O. Forster and H. E. Pierz.
- FRIDAY, 5th.—Royal Institution, 9. "Problems underlying Nutrition," by Prof. Henry B. Armstrong, F.R.S.
- SATURDAY, 6th.—Royal Institution, 3. "Moulds and Mouldiness," by Prof. Marshall Ward, F.R.S., &c.

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THE CHEMICAL NEWS.

VOL. XCI., No. 2371.

A DETERMINATION OF THE AMOUNTS OF NEON AND HELIUM IN ATMOSPHERIC AIR.*

By Sir WILLIAM RAMSAY, K.C.B., F.R.S.

SOME time ago I communicated to the Society the results of an attempt to estimate the amounts of krypton and of xenon in air (*Proc. Roy. Soc.*, vol. lxxi., p. 421). The quantities were necessarily minimum estimates, for there is no doubt that both krypton and xenon must evaporate when air evaporates, even if that take place at a very low temperature. Dr. Travers and I guessed at the amounts of neon and helium, and supposed that the amount of helium was one or two parts per million, and that of neon one or two parts per 100,000. This guess is not very far from the truth, as the following account of recent experiments will show.

The ingenious method discovered by Sir James Dewar of using cooled cocoanut charcoal as an absorbent for gases has made it easy to carry out the estimation. The process consists in cooling 100 grms. of such charcoal to -100° , approximately, in a bulb from which all air has been removed by a pump. Such charcoal will absorb about three litres of air; at that temperature neither neon nor helium are absorbed in appreciable quantity, as special experiments showed. Hence on placing the cooled bulb containing the charcoal in communication with a Töpler pump, the uncondensed gases enter the barrel of the pump. On closing the connecting stopcock, a further quantity of gas accumulates, and is again removed into the pump in the same manner. As the relative volumes of the pump and of the cooled bulb were approximately 4 to 1, after communication had been established four times, only 1/256 of the contents of the bulb were left in it. And as the gas in contact with charcoal exerts a kind of vapour-pressure, inasmuch as the pressure which it gives depends on the temperature as well as on the extent of the surface of charcoal to which it is exposed, it may be assumed that gas escapes from the charcoal on each reduction of pressure, and that the more volatile gases in the bulb should be expelled by the less volatile.

In this manner 18 litres of moist air were treated; on its way to the charcoal bulb it traversed a tube filled with phosphorus pentoxide, to deprive it of moisture. The temperature was about 15° during these operations, hence the actual volume corrected to 0° C., and deprived of water-vapour, was about 16,800 c.c. This volume was reduced to about 400 c.c. in the manner described, and the smaller volume contained practically all the neon and helium.

By means of a smaller apparatus containing about 3 grms. of charcoal, the volume was further reduced, in a similar manner, until only a few c.c. were removed through the pump. A convenient cooling mixture was found to be frozen ether. By stirring ordinary commercial ether with a test-tube containing liquid air, and frequently replenished, solid ether at last begins to coat the outside of the test-tube. At this stage liquid air is poured on to the surface of the ether, and a crust of ether-ice forms. This is broken, and stirred through the liquid portion, and the operation is repeated until a sufficient quantity of solid has accumulated. The cold ether bath may now be used to cool the charcoal tube; not much solid melts during the process, and the temperature registered by a pentane thermometer was approximately -100° .

Having reduced the volume of the gases to about 2 c.c., the remaining oxygen and nitrogen were removed by sparking. It is true that about 2,100 of a c.c. of argon may be thus retained; but the quantity is probably much less, for oxygen is less volatile than argon, and would probably remove at least a portion. The residue, at any rate, did not show the argon spectrum.

The inert residue was then, after it had been measured, admitted into the small apparatus; the charcoal, however, was now cooled with liquid air. Preliminary experiments had shown that at that temperature, neon is retained by charcoal in considerable amount. Hence, on opening the stopcock communicating with the pump, helium escaped, while neon was retained. The surface of the charcoal was very large considering the small quantity of gas presented to it. As before, the pump was opened four times, so as to make sure that all helium should escape. This helium showed the neon spectrum but feebly; it may have contained a few per cent of neon. On the other hand, the neon remaining in the charcoal, when expelled by heat, was almost free from the helium spectrum. Probably then, the estimate which will be given errs in that the quantity of helium may be somewhat too large, and that of neon too small. The neon was again purified by sparking before being measured; for it was thought best to jacket the charcoal tube with the vapour of boiling quinoline (237) in order to make sure that all neon had been expelled, and the effect was to expel along with it some nitrogen which had remained in the charcoal, besides some carbon dioxide.

A word may be said as to the method of measuring very small quantities of gas. The measuring tube was provided with a two-way stopcock, one exit from which was sealed to an inverted syphon of capillary tubing. It had also two points of blue glass sealed in, one indicating the volume 2.409 c.c., the other 9.657 c.c. The smaller volume was alone used. In reading the volume of the gas, the measuring tube is clamped in front of a long standard scale (one by Zeiss, which had been calibrated). The mercury is then set to the blue glass point, by lowering the mercury reservoir attached to the measuring tube, and the temperature and difference in level of the two mercury surfaces are read. The volume at 0° and 760 m.m. pressure was calculated in the usual way.

The excellent results given by this method will be seen from the correspondence between the volume of mixed neon and helium, and the sum of the measurements of each separately.

Volumes of Neon and Helium.

Volume of mixed gases, after sparking ..	0.2756 c.c.
" helium, unsparked	0.0685 "
" neon, after sparking	0.2080 "

The sum of the last two is 0.2765—a number agreeing within 1 per cent of the volume taken.

Referring these quantities to the volume of air from which they were extracted, and also to that of the argon in that air, we obtain—

Neon in air ..	1 volume in 80,790 volumes of air.
Helium in air ..	1 " 245,300 " "
Together ..	1 " 61,000 " "

The percentage of argon in air being taken as 0.937, there follows—

Neon in argon ..	1 volume in 757 volumes of argon.
Helium in argon ..	1 " 2300 " "
Together ..	1 " 571 " "

The percentages by weight and volume are as follows:—

Neon by weight in gaseous air ..	0.0000086 per cent
Neon by volume in gaseous air ..	0.0000123 "
Helium by weight in gaseous air ..	0.00000056 "
Helium by volume in gaseous air ..	0.0000040 "

The density of crude argon was determined by Lord Rayleigh and myself as 19.94; the mean density of pure argon, in conjunction with Dr. Travers, as 19.957. It is

* A Paper read before the Royal Society, March 16, 1905.

interesting to see whether, neglecting the heavier constituents (inasmuch as their amount is inappreciable), the calculated and found densities of argon agree. Allowing for the presence of the neon and helium, the density of pure argon should be 19.953; the most reliable numbers found by Travers and myself were 19.952 and 19.961.

One more point deserves notice. A fair quantity of the mixture of neon and helium was prepared by liquefying air; 540 c.c. of liquid air were collected. The lighter gases were collected by blowing air through this liquid and collecting in a gas-holder. This mixture was then fractionated by absorption in charcoal, as already described, but the charcoal was cooled with liquid air to -192° ; the mixed gases measured 4.463 c.c. Now, taking the density of liquid air as 1, the total volume of the gaseous air from which the 540 c.c. of liquid air had been obtained was 404.4 litres at 0° and 760 m.m.; and the proportion of mixed gases in gaseous air would be 1 in 90,000. A considerable quantity of neon, and possibly a trace of helium, had apparently been retained by the charcoal. But the yield on a large scale is not a bad one; and no doubt, if the charcoal were cooled not below -100° , all the gases could be extracted.

Now this gas must have contained all the free hydrogen present in the air; and it was mixed with oxygen and sparked for a short time; it was then collected through the pump, which dried it, and it was re-measured. There was no contraction; the volume of the mixed gases plus added oxygen was 5.169 c.c., and that of the same gas after sparking 5.170 c.c. The amount of free hydrogen in air, therefore, must be less than 1/500 of the volume of the combined neon and helium, assuming it to be possible to measure to 0.01 c.c. It should be added, perhaps, that it would be well not to regard this experiment as conclusive, but it is given for what it is worth.

PERMEABILITY OF QUARTZ VESSELS.

By M. BERTHELOT.

THE use of quartz vessels opens up an interesting question regarding their permeability. In fact such vessels are not impermeable to gases and vapours in the same way as glass vessels, which latter under ordinary conditions are absolutely impermeable to ponderable matter.

Observations hitherto have been made by M. Villard (*Comptes Rendus*, vol. cxxxviii., p. 1033) and by MM. Jaques and Perrot for helium (*Comptes Rendus*, vol. cxxxix., p. 789) at temperatures below red heat.

I have also found the same thing to be true, though in a less degree, for nitrogen and oxygen, and investigated the diffusion taking place between the gases contained in quartz tubes and atmospheric gases under certain conditions.

All the tubes which were used for these experiments were heated in an atmosphere of atmospheric air under normal pressure. The tubes were exhausted by the mercury pump in such a manner that the gas could be subject to an exactly known pressure without the least trace of mercury entering.

I then performed the following experiments:—

1. *With Amorphous Carbon* (wood charcoal purified at red heat by chlorine, &c.).—A few m.grms. were deposited in a tube of capacity 5.5 c.c. A vacuum was then made by the mercury pump in order to extract all the occluded gases, the tube being heated during exhaustion before sealing. When the vacuum was as perfect as possible the tube was sealed.

It was then maintained at a temperature of $1300-1325^{\circ}$ for half-an-hour. It was then slowly cooled to ordinary temperatures, and opened over mercury. There was no longer a complete vacuum, but the tube contained gases exerting a decided pressure, though much less than that of the atmosphere, proving no possibility of a direct com-

munication. In fact the volume of these gases reduced to atmospheric pressure represented only 1.5 hundredths of the capacity of the tube. This gas consisted of:—

N	0.9 part
CO	0.6 „

The nitrogen comes from the air direct, whilst the carbon monoxide is formed from the atmospheric oxygen and the carbon. It is evident that the elements of the air penetrate by osmosis during the experiment.

2. *Amorphous Carbon* (wood charcoal purified by chlorine).—Nine m.grms. of material were used in a tube of 29 c.c. capacity. The tube was filled with pure nitrogen, and heated for some moments over a flame, then the tube was exhausted until the pressure was reduced to 160 m.m.; i.e., to about one-fifth of the atmospheric pressure, a mercury pump being used. The tube was then sealed and heated to 1300° for one hour. The internal pressure became under such conditions 1.3 atmospheres and the softened tube became swollen. On cooling it was opened over mercury. The volume of gas extracted, reduced to atmospheric pressure, was 7.3 c.c.; that is increased by one-fifth of the initial volume (6 c.c.). The gas was found to consist of 82 per cent nitrogen and 18 per cent carbon monoxide. As a control experiment a glass vessel of nitrogen which underwent the same exhaustion was attached to the pump. On analysis this latter contained not a trace of oxygen. The formation of carbon monoxide, and also the increase in volume of the gas, points to the fact that the oxygen penetrates by osmosis.

3. *Pure Oxygen* (introduced into a tube of 4 c.c. capacity).—The pressure in the tube was reduced to one-half the atmospheric pressure. The tube was then sealed and heated for one and a-half hours to 1300° . At the end of the experiment the tube was opened over mercury. Three per cent of nitrogen was found which had entered by osmosis.

4. *Hydrogen*.—Several experiments were made with tubes containing hydrogen, the experiments confirming the facts shown above. I will quote the following as an example:—

Pure hydrogen was contained in the tube under an initial pressure of 152 m.m., atmospheric pressure being 751. The capacity of the tube was 5 c.c., and it was heated for one hour at 1300° C. The gas finally extracted had volume 0.68 c.c. under atmospheric pressure (as against 1 c.c. of initial volume). The final gas contained 0.12 c.c. of nitrogen.

These numbers show that for 100 volumes of hydrogen 44 have disappeared (by transpiration or the action of the oxygen), and 12 volumes of nitrogen have entered the tube, only about one-half of the initial hydrogen remaining in the tube.

5. *Carbon Dioxide*.—In the case of carbon dioxide the penetration of the nitrogen was very slight.

6. *Oxygen*.—The amount of penetration of oxygen into nitrogen is very doubtful. An investigation of the hydrogen carbides under similar conditions give very interesting results, which will form the subject of a future research.

I am now limiting myself to one or two isolated cases relative to the diffusion of hydrogen and progressive penetration of the oxygen of the air. I chose naphthalene on account of its high stability and formene on account of the simplicity of its composition.

7. *Naphthalene*.—0.051 grm. was placed in an empty tube of about 5 c.c. capacity, and heated to 1300° . The tube exploded. This fact may be explained by the considerable increase of volume, owing not so much to the vapour of the naphthalene as to the hydrogen resulting from its decomposition.

8. *Naphthalene*.—This time 0.021 grm. was placed in a tube of capacity 4 c.c., and heated to 1300° for one hour. The tube did not explode, and was found full of carbon. This carbon contained no more naphthalene. If all the hydrogen had been liberated (0.0013 grm., equivalent

to about 14 c.c. in the cold), the pressure at 1300° would have been increased to 17 atmospheres, and the tube would have exploded. However, at the moment when the tube was opened under mercury, owing to the shaking produced by the filing off of the point and the rapid change of pressure, the tube cracked, or rather became divided, into large fragments, of form and dimension very different from those formed during the explosion.

The gas extracted under these conditions reduced to atmospheric pressure occupied only 0.18 c.m. (instead of 14 c.m. of the carbide), and contained:—

Nitrogen	0.15 c.c.
Hydrogen	0.03 ..

These facts show that the decomposition of naphthalene into its elements from ordinary temperatures up to 1300°, and during the period the tube is maintained at 1300°, does not take place rapidly but very gradually, during which time the hydrogen slowly diffuses through the tube burning outside. A little nitrogen penetrates the vessel, which mixes with the small quantity of remaining hydrogen, occupying on cooling scarcely a twentieth of the capacity of the tube.

9. *Pure Formene* gave analogous results, and still more characteristic. At an initial pressure of 1373 m.m. (about half an atmosphere) the formene occupied 4.5 c.c., and was heated for one hour to 1300—1325° C.

At the end of the experiment the tube was filled with carbon, and the volume of the residual gas was found to be 2.97 c.c.; that is, more than the initial volume of 2.25 c.c. when reduced to atmospheric pressure. The gas was quite free from oxides of carbon, and contained:—

Hydrogen	2.72 c.c.
Formene	0.05 ..
Nitrogen	0.20 ..
	2.97

Considering the initial pressure of the formene, 4.5 c.c. of hydrogen should have been obtained. It shows therefore that one-third of the hydrogen has diffused or been burnt; the formene having almost completely disappeared.

10. *Pure Formene*.—In a second experiment at initial pressure 360 m.m. (atmosphere pressure, 756 m.m.) and tube capacity 4 c.c., the tube was raised to 1100° in the course of about half-an-hour, then cooled, and examined without opening. It was filled with free carbon as in the above experiment. The next day it was again heated for one hour, and the temperature increased to 1300°, and then maintained for one hour at this temperature. On cooling, the tube had become white and transparent, no trace of carbon being observed.

I first thought that the tube must have been perforated so that air had entered directly which had burnt up the carbon. A further examination of the tube showed this hypothesis to be wrong. Indeed, on opening over mercury two hours after, the pressure was found to be very little over half the atmospheric pressure; that is, almost what it was to start with. This excluded any possibility of a perforation which must have established equilibrium of pressure during the long period of cooling. The tube contained 2.12 c.c. of gas, consisting chiefly of nitrogen with a little oxygen and carbon dioxide. These facts show that the air must have penetrated little by little by osmosis during the second part of the experiment.

Two volumes of formene, or rather of carbon and the corresponding hydrogen, were burnt little by little as much outside the tube as in its interior. We see by these experiments that it does not do to indefinitely prolong the heating of quartz vessels.

We also see that melted quartz on solidification behaves respecting gases up to a certain point as an animal membrane susceptible of endosmosis and exosmosis. The order of these phenomena depend on the thickness of the wall, on its hardness, the adherence of the carbon or the other solid products of the reaction to the walls, to the

amount of alkali united with the silica, and the successive temperature reached, besides the duration of each temperature. Finally, the amount of action depends on the opposition which exists between the constant composition of the external air and the variation of composition of the gases resulting from the gradual reactions of the oxygen on the combustible bodies (hydrogen and carbon); that is, in the composition and to the variable tension of the internal gases.—*Comptes Rendus*, vol. cxi., No. 13, p. 821.

THE COMPOSITION OF SLAGS OBTAINED IN THE MANUFACTURE OF FERRO-MANGANESE.

By F. WITTMANN.

THE general opinion on the question as to what are the best slags to produce in the manufacture of ferro-manganese is that these slags should be as basic as possible. But the ideas held by different experts as to the basicity of a slag are very variable; and, consequently, the calculation of the slags and of the charges to be used to obtain ferro-manganese leads to very different results. Theoretically, the most basic slag is the one in which the ratio of the oxygen in the acids (amongst others, the silica) to the oxygen of the bases is the smallest. But the part played by alumina being very badly defined, it is sometimes looked upon as an acid and sometimes as a base, while some workers do not pay any attention to it at all.

In other cases, again, the basicity of the slag is calculated according to the method of Platz—taking, on the one hand, the whole of the silica and the alumina, and, on the other hand, the whole of the remaining bases, and finding the ratio of these results. The most basic slag is the one in which the ratio is the smallest. Finally, the practical man calls the most basic slag the one with an earthy fracture, and which is the most difficultly fusible. He supposes that there is a constant relation between the fusibility of a slag and its chemical composition, while in reality such is not the case.

But in spite of this, the determination of slags from their fused appearance is the most convenient way of controlling the working of ordinary blast-furnaces, for in these cases the only thing to make sure of is the formation of an effective slag practically in the same time that it takes to melt the reduced iron.

The conditions are quite different, however, when we have to do with the production of ferro-manganese. The slag is at the same time a solvent of protoxide of manganese, and its greater or lesser value depends on its absorbing power for this oxide, and not on its fusibility. The return of manganese (losses of metal by the mechanical action of dust being put on one side) depends first of all on the quantity of coke consumed; thus by using enough coke we can obtain a slag rich in silica and rather poor in manganese. Inversely, in the manufacture of spiegeleisen, we can scoria a large proportion of the manganese, even when the slag contains a large excess of bases, by diminishing the amount of coke used.

The publication of the results of analyses of slags obtained in the manufacture of ferro-manganese is consequently without any interest if it is not accompanied by an account of the other conditions of manufacture.

For the same proportion of manganese, the composition of the slags is indicated in such a variable manner that, if we took no notice of the consumption of coke, we should be led to most different opinions. To be able to determine the best slag in a given case, it is necessary only to compare slags obtained under general conditions (regularity of the consumption of coke, temperature of the blast, shape of the furnace, &c.) as closely as possible. In a word, slags can only be compared one with another when they have been obtained from the same blast-furnace.

Order No.	Analysis, per cent.							Index of basicity calculated				Remarks			
	Mn.	SiO ₂ .	Al ₂ O ₃ .	FeO.	CaO.	MgO.	BaO.	With MnO.		Without MnO.					
								After Mrazek.	After Platz.	d.	b.		After Mrazek. $O_d : O_b = 1.$	After Platz. $SiO_2 + Al_2O_3 = 1.$ ΣRO	c.
												Percentage of Mn in the ferro-manganese obtained.	Date of manufacture.		
1.	23.33	29.02	7.05	0.48	37.03	1.89	—	0.67	1.30	1.74	0.96	1.09	38.92	80	Aug., 1893
2.	22.25	29.70	8.33	0.72	34.30	2.05	1.51	0.77	1.26	1.60	0.94	1.01	37.86	70—75	April, 1895
3.	21.09	30.15	7.97	0.56	34.43	3.00	1.88	0.79	1.24	1.60	0.95	1.05	39.31	55—60	July, 1894
4.	19.69	29.55	8.91	0.29	37.30	2.05	1.10	0.96	1.30	1.57	1.01	1.06	40.45	80	April, 1895
5.	19.18	30.25	6.78	0.52	39.14	2.34	0.19	0.90	1.23	1.65	0.96	1.14	41.67	50, 70, 80	April, 1894
6.	18.50	30.60	7.87	0.43	37.55	2.41	1.21	1.19	1.22	1.56	0.96	1.08	41.47	55—60	April, 1895
7.	14.78	30.25	8.32	0.46	39.25	4.65	—	1.32	1.27	1.53	1.06	1.15	43.90	80	Oct., 1890
8.	14.33	31.47	8.31	0.62	38.33	3.29	2.85	1.15	1.19	1.49	0.99	1.13	44.45	40	July, 1894
9.	13.96	29.25	8.58	0.86	44.01	3.34	—	0.55	1.37	1.64	1.17	1.27	47.35	30—50	Aug., 1899
10.	13.79	30.37	10.59	0.61	43.82	2.15	—	0.42	1.34	1.47	1.15	1.14	45.97	80	July, 1899
11.	12.17	30.91	8.26	0.59	41.62	2.08	—	0.63	1.26	1.54	1.09	1.23	47.70	80	Jan., 1894

In the accompanying table will be found some analyses of this class of slag. They all came from the same blast-furnace, and cover a period of nine years, and are all the complete analyses made during this period.

In columns *a* and *c* we calculated according to Mrazek the ratio between the oxygen of the acids and that of the bases, and in columns *b* and *d* the ratio of the silica and alumina to the other bases according to Platz. In columns *c* and *d* we find the same calculations made under the supposition that the slag is free from manganese. In all these cases we have neglected the sulphur. The comparison of the different indices of basicity thus obtained shows that they do not explain in the slightest degree the lowering of the proportion of manganese present in the slags. However, we ought to remark that, in the blast-furnace in question, the consumption of coke, compared with the number of tons of the alloy obtained, was practically constant. Further, we almost always employed the same qualities of iron and manganese ores during the period of manufacture under consideration. On the other hand, if we compare the proportion of manganese with the total amount of CaO + MgO + BaO, we see that the concordance (shown in column *e*) is surprising. The same concordance exists if we compare the proportion of manganese in 100 parts of the earthy oxides; this shows distinctly that the amount of manganese is influenced by the addition of lime to the slag.

If we construct a curve—one axis showing the proportion of manganese and the other the proportion of CaO + MgO + BaO—we see distinctly that the proportion of manganese diminishes very rapidly at first, and up to a certain point the lime is of no use, but from that point the curve becomes almost horizontal. We must again remark, however, that this curve is only useful for certain conditions of working. The increase in the quantity of coke consumed would apparently have the effect of displacing the curve lower and to the left.

Admitting that ferro-manganese of high percentage requires, on account of its high proportion of manganese, a large amount of coke per ton of alloy, the consumption of coke for alloys of different percentages should not be estimated in absolute figures. We should take the sum of the amounts of coke required respectively by the iron and the manganese. If the iron requires, for example, 100 per cent of coke and the manganese requires 25 per cent, a ferro-manganese at 50 per cent would require $\frac{100}{2} + \frac{25}{2} = 155$ per cent. A consumption higher or

lower than the figure thus calculated indicates a change in the working of the blast-furnace, which consequently destroys the regularity of the curve.

The results of the present research may be summed up as follows:—

1. The best composition of slag for the production of ferro-manganese cannot be calculated by the methods of Platz or of Mrazek. In the same way, the fusibility of the slag cannot be taken as an indication of the best composition of the slag.

2. The only characteristic which determines the quality of the slag is the sum of the CaO + BaO + MgO, the constituents being expressed in percentages of the slag wished for.

3. There always exists, under determined conditions, a point where the addition of further quantities of lime becomes useless, and even disadvantageous, on account of the infusibility thus communicated to the slag and the loss of material that results.—*Stahl und Eisen*, 1904, p. 14.

Phenanthrene Hydrides.—Pierre Breteau. — The author prepares several phenanthrene hydrides by applying MM. Sabatier and Senderens' method of hydrogenation to this carbide. This research is especially concerned with the preparation and investigation of the properties of the hexahydride C₁₄H₁₆, and the octohydride C₁₄H₁₈.—*Comptes Rendus*, cxl., No. 14.

RESEARCH ON COLOURED GLASSES.

By AD. LECRENIER.

No distinction is made as a rule between the metallic oxides from the point of view of the colouration they impart to glass or crystal. The colouring process differs, however, completely with the different oxides. For example, the reason of the pink colouration of crystal by gold is quite different from that of the blue colouration of the same crystal by cobalt oxide; and the yellow colouration of glass by compounds of silver is produced by a process equally different from either of the former. By a close investigation of the cause of the different colourations and the conditions under which they are produced, I have been led to class the oxides and other colouring agents into three distinct groups: immediate colouring agents, those of saturation, and those of cementation.

I. Immediate Colouring Agents.

These colouring agents produce in glasses shades whose intensity is in direct relation to the proportion in which they are used. To this group belong the following oxides and other compounds:—Cobalt, nickel, ferric, cupric, ferrous, chromic oxides, chromic anhydride, manganous, manganic, uranium oxides, the sulphides, and selenides of the alkalis and alkaline earths.

These bodies impart a certain colouration to glass, whatever be the proportion, and the colour obtained serves, under identical conditions of composition and thickness of the glass, as a colorimetric estimation of the proportion of oxide incorporated.

I say "under identical conditions of composition of the glass," because the shades may vary according to the chemical nature of the coloured glass. They are, for example, different for the same oxide, according as it is a soda or potash glass, or even according to its basicity.

II. Colouring Agents of Saturation.

The colour imparted by the products in this category only appears above a certain limit, and generally only under certain conditions of temperature.

To this group belong cuprous oxide, compounds of gold, silver salts, stannic oxide, phosphates, arseniates, and fluorides.

It is not enough, for example, to incorporate in the glass any quantity whatever of cuprous oxide in order to obtain a red colouration. On the contrary, the glass remains absolutely colourless until a certain limit is reached, varying according to the chemical composition of the glass. When the minimum limit is reached, the glass becomes red, and the colouration obtained is immediately very intense, so that it is practically impossible with cuprous oxide to obtain a glass uniformly coloured, and presenting, according to the proportion of the colouring agent, a continuous gradation from pale pink to opaque-red. With cobalt oxide, on the contrary, taking an example from the previous group, it is possible to obtain, according to the proportion, all shades of blue, from the shade which is only visible in glass of a considerable thickness up to such a depth that the true colour can only be seen in layers of extreme thinness.

Certain authors attribute the colouration of copper glass to the presence of metallic copper, others to the presence of cuprous oxide. I agree with the opinion of the latter for the following reasons:—

1. Copper glass cooled suddenly on leaving the crucible is absolutely colourless; it only acquires its ruby-red colouration after having been cooled, then re-heated or cooled slowly when the content of cuprous oxide is great enough.
2. The colouration is produced with a proportion of cuprous oxide which decreases as the basicity of the glass increases.
3. All the copper salts are colourless.
4. Cuprous oxide is fusible and ruby-red.

It appears to me conclusive from these facts that colourless copper glass contains copper in the state of copper silicate, and that the appearance of the red colouration on re-heating would be due to dissociation of copper silicate into silicic anhydride, which would become associated into the more complex molecule of a poly-silicate and into free red cuprous oxide.

The colouration of glass by gold does not occur until the amount of the colouring agent reaches a certain proportion. The shade obtained is not so deep, and is not generally so rapidly produced as in the case of cuprous oxide. The process of colouration is not yet clearly understood; it is in every case more complicated than that of the colouration by cuprous oxide. It appears, moreover, that the colouration is due to a precipitation of metallic gold in particles, which, in filtering the light, produce different colours, according as the free spaces between them correspond to the different wave-lengths of light.

The colour most frequently produced with gold is purple-red, but it is possible to obtain with this metal by re-heating the glass, and under certain conditions of temperature, of fusion, and composition of the glass, not only red-purple, but violet, blue, green, yellow-brown; in fact, nearly all the colours of the spectrum.

M. Spring has demonstrated further that the clearest pink glass coloured with gold, when illuminated by a very strong ray of light, shows a brown colouration by reflection, which is only due to the presence of particles of metallic gold.

In the class of colours of saturation may be included the opalisation produced in glass by the introduction of phosphates, arseniates, and fluorides.

This opalisation is only produced with a minimum of the colouring agent, and under conditions that we shall give special consideration to later.

III. Glasses Coloured by Dyeing or by Cementation.

The colouration of glass in yellow or ruby-red may be obtained by causing to penetrate into the substance of the solidified and moulded glass certain bodies applied to the surface, by heating the glass thus treated to a temperature considerably below that of its fusing point.

A yellow stained glass is obtained with silver by covering the piece to be stained with a plaster made of an inert powder; for example, red ochre mixed with a greater or lesser proportion of the chloride or sulphide of silver. This mixture is ground under water, and applied with a brush, and, after drying, the piece is moderately heated to dull redness in a painting oven; after being cooled, the plaster is removed by washing with water. Examination of the surface of the glass after this operation proves that it has lost nothing of its brilliancy nor of its former appearance, but the glass has acquired a yellow colour, which has penetrated to a certain depth into the interior.

The red stain is obtained in a similar manner. The glass is plastered with a mixture of ochre and copper oxide. After drying, the glass is baked in the oxidising atmosphere of a painting oven; the glass is then washed and freed from its copper plaster; its appearance is unchanged, but it is stained a light yellowish green.

In order to obtain a deep red shade, the glass must be re-baked, but this time in a reducing atmosphere; that is to say, in a completely closed oven, in which a reducing gas is generated by introducing a certain amount of coarse charcoal. Under these conditions, the cupric oxide, which penetrated into the glass at the first baking, is reduced to the cuprous condition, and imparts an intense red colour to the glass.

Molecular Exchanges.

When several oxides, or colouring compounds, simultaneously enter into the composition of a glass, there may be produced, according to the physical conditions in which the latter is situated, interesting molecular exchanges. The most common are those which occur between the oxides of iron and manganese. The primary substances, the purest, which enter into the

formation of the glass, all contain small quantities of ferruginous products, which, after fusion, impart a yellowish green tinge to the glass, which is made to disappear by incorporating into the composition of the glass a certain quantity of manganese dioxide, always on this account called *glass-makers' soap*. Much has been written on the theory of this process. Some see in the action of the manganese only a physical action consisting in the extinction of the yellowish green colour of the iron by the complementary violet colour introduced by the manganese. Others consider this action purely chemical, an oxidation of the highly coloured ferrous or ferroso-ferric oxides, and their transformation into very pale reddish yellow ferric oxide. Others, again, believe in the existence of both causes, but do not bring any decisive proofs to the support of their views.

I consider, however, that the last theory is the most plausible, for the following reasons:—Iron imparts very different colours to glass, according as it enters into its composition as ferrous oxide, ferric oxide, or as a mixture of these two oxides.

Several years ago I prepared for Dr. Zsigmondy some glass containing 1 to 2 per cent of iron in a ferrous state. To the ordinary constituents of calcium-soda glass of the formula $6\text{SiO}_2\text{Na}_2\text{O}\text{CaO}$, prepared without any oxidiser, I had added iron in the form of ferrous oxide, with a slight addition of acid potassium tartrate, and in order to avoid all possibility of oxidation I carried out the fusion in a completely closed crucible, the cover of which was pierced with two holes, one for the introduction and the other for the exit of the current of inert gas. Hence the fusion and refinement of the glass took place in an absolutely reducing atmosphere.

This glass, which constitutes the adiantum glass of Zsigmondy, has a blue, very slightly greenish tint. It is thus proved that iron, entirely in the ferrous oxide state, produces a blue colour in glass. On the other hand, when by means of suitable reagents we succeed in maintaining the iron in an altogether ferric condition, a red-brown colour is obtained. By mixing the two oxides, according as one or the other predominates, bluish green, green, or yellowish green tints are obtained.

Glass obtained by the simple fusion of primary materials, sand, soda, potassium, or sodium nitrate, and lime, without the addition of a colouring agent, has a yellowish green shade, even if the ferruginous compounds which occur as impurities are exclusively in a ferric state.

By employing even a very considerable quantity of nitrate in the mixture, it is impossible to produce a pure yellow glass. From what we have just seen on the subject of the colour of iron silicates, we must certainly admit that in this crude glass there is iron in a ferroso-ferric state.

The ferric oxide has therefore been partially reduced to a ferrous state. How comes this reduction? Because the stable form of the fused iron silicate is ferrous silicate. Hence it follows from the researches of Muller that, if ferric oxide is introduced into glass, there is loss of oxygen; and the more acid the glass the greater the decomposition.

Further, the experiments of Percy have proved that the stable form of fused iron silicate is a minimum of silicate. The experiments made with a view to obtaining a ferric silicate by heating together silica and ferric oxide have not succeeded; they resulted in a mixture of ferrous silicate, ferroso-ferric oxide, and uncombined silica. Hence if during the decomposition of the nitrate by heat the iron changed completely into a ferric state, it would again be partially brought back to a ferrous condition in consequence of its final combination with silica.

What now takes place if manganese dioxide is introduced into the glass? The dioxide at red heat decomposes according to the formula—



Therefore, by means of heat alone, one-third of the manganese is reduced to a manganous state. Consequently, the manganese introduced into the glass changes partly

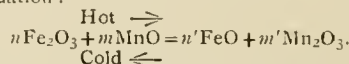
into manganous silicate, and the larger part changes into manganic silicate. The manganous silicate imparts an extremely pale pink tint to the glass, which may be quite ignored, in comparison with the violet-red shade of the manganic silicate, the intensity of which is so great that a proportion of 6 to 7 per cent makes the glass completely black.

(It is possible that, manganese being the analogue of iron, part of the manganic oxide is reduced to the manganous state in consequence of its union with silicic anhydride, but this is of no importance from the point of view of the proposition I wish to establish.)

The manner in which the decolouration is made is very simple; if by a trace of cobalt a slightly bluer tone is imparted to the violet produced by the manganese, the complementary yellowish green of the iron is masked. But glass-makers know that glass taken from the crucible and cooled rapidly has, when the proportion of manganese is well adjusted, a pink shade which it loses entirely on re-heating.

How can the disappearance of the pink colour be accounted for? It is caused, as I have already explained, by the presence of the following four colouring oxides: Ferrous oxide, ferric oxide, manganous and manganic oxide.

We may suppose that a state of chemical equilibrium is established between these oxides, determined by their respective amounts and the temperature of the glass, the oxygen acting more or less on the iron or on the manganese, according to the thermal conditions of the glass, according to the equation:—



When hot the ferric oxide gives up its oxygen to the manganous oxide; when cold, or rather during gradual cooling of the glass, it is the manganic oxide which gives up its oxygen to the ferrous oxide. It is the latter reaction which occurs during re-heating and which causes the disappearance of the primitive pink tint of the glass.

When the glass is removed from the crucible it rapidly congeals; the state of the iron and manganese at the fusion point remains fixed by this rapid solidification, and the pink colour gives evidence of the action of oxygen upon the manganese. In the same way in steel work, rapid cooling establishes the brittle character which the steel acquires at red heat, whilst gradual cooling, allowing a slow action of the molecules, would have allowed it to acquire the ductility of untempered steel; in the same way slow cooling in re-heating ovens allows the exchange of oxygen to take place.

In common with most phenomena of chemical equilibrium, the one in question is influenced by the different physical agents. We have just investigated the influence of temperature; that of light is also interesting to note.

The glass, decolourised in the re-heating oven, when exposed to an intense actinic light, resumes a pink tint similar to that before being re-heated. A second re-heating may cause it to lose this tint again, and so on. This re-colouration of the glass under the influence of actinic rays (X-rays act similarly to light rays) corresponds therefore to a reduction of the ferric oxides. We note, in passing, that in liquids the same phenomenon of reduction is observed with ferric salts in solution or in suspension in presence of reducing agents, or under the influence of light. Therefore actinic radiations have a distinctly decomposing action on the ferric compounds which they encounter.

Atmospheric pressure also exercises a very distinct action upon the state of chemical equilibrium that we are investigating. I had occasion to note this fact in all the experiments I made in studying glass refining by Lepersonne's process. This process, as is well known, consists in creating a vacuum in the crucible whilst refining the glass. Under a great reduction of pressure, the bubbles of carbonic acid and other gases, which only free themselves very

slowly from the fused mass during the refining, suddenly acquire a considerable volume, and hence a great increase of force, which facilitates their evolution. Under these conditions the refining is reduced from several hours to a few minutes.

The influence of decreased pressure upon the oxygen displaceable from ferric and manganic oxides is such that I have found impossible by ordinary means to compensate for the yellowish green shade of the ferrous-ferric oxides by manganese; the latter seemed under these conditions to be completely reduced to the manganous state.

It is well to note that manganic oxide is not the only compound capable of imparting oxygen to ferrous oxide dissolved in the glass. Arsenic anhydride and antimonic acid act in the same manner, and therefore have a certain influence on the phenomenon of glass decoloration.

Glasses containing Sulphides of the Alkalis or Alkaline Earths as well as Oxides of the Heavy Metals.

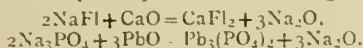
As we have previously seen, sulphides of the alkali and alkaline earth metals impart a colour to glass which varies from a pale golden yellow to dark brown, according to their proportion. If, at the same time, we dissolve in the glass an oxide of a heavy metal—for example, the oxide of copper or lead—we obtain a glass which on leaving the crucible presents exactly the same colouration as without the heavy oxide; but if, after the glass has been allowed to cool, it is again brought to the fusion point, we notice that the colour gradually deepens, becoming finally perfectly black and opaque. The reaction which takes place under these conditions is easy to understand. When hot we have present $\text{Na}_2\text{S} + \text{PbO}$, and on re-heating the following reaction takes place:— $\text{Na}_2\text{S} + \text{PbO} = \text{PbS} + \text{Na}_2\text{O}$.

The proof of this is that if the non-reheated yellow glass is dissolved in hydrofluoric acid there is a copious evolution of sulphuretted hydrogen, whereas by using the glass blackened by re-heating, this discharge does not take place; moreover, the lead sulphide is reproduced at the end of the reaction.

Opalised Glasses.

The opalisation of glass is produced by the introduction of phosphates, arseniates, and fluorides into the mass. As I have previously stated, opalisation does not begin to be apparent until a certain limit is reached, below which point the glass remains clear, whatever may be the conditions of temperature to which it is submitted. When the quantity of the opalising agent is sufficient to exceed the limit of saturation, the glass still remains transparent as long as it is at fusion point; it is only by slow re-cooling, if the proportion of the opalising body is very great, or by re-cooling and final re-heating, that it attains its opacity.

It seems that in fused transparent glass phosphoric and arsenic acids remain combined with the alkalis, and that opalisation takes place by one of the following reactions:—



—*Bulletin de la Société Chimique de Belgique.*

COLOUR REACTIONS OF PYRUVIC ACID
WITH α - AND β -NAPHTHOL IN SULPHURIC
ACID SOLUTION.

By Dr. EUGENIO PINERUA ALVAREZ,
Professor at the University of Madrid.

THE sulphuric acid solution of α - and β -naphthol in presence of pyruvic acid produces phenomena which not only allow of our characterising and distinguishing the latter acid from all other organic acids, but also enables us to distinguish between the two phenols already mentioned.

The reagent used was proposed in 1897 by the author of the present note, in order to examine organic acids, and consists of a fresh solution of α -naphthol or of β -naphthol

(0.02 to 0.05 grm.) in sulphuric acid (1 c.c.) of specific weight 1.83. (See *Comptes Rendus*, Feb. 8, 1897; *CHEMICAL NEWS*, 1897, vol. lxxv., p. 61; *La Gazz. Chim. Ital.*, Feb. 26, 1897; *Pharmaceutische Centralhalle de Dresden*, March, 1897).

If to ten drops of the reagent one drop of the organic acid is added, and, after having been mixed cold in a porcelain dish, the mixture is gently warmed by a spirit lamp, the following colourations are successively seen:—

1. *With the Sulphuric Acid Solution of β -Naphthol.*—The reagent when cold assumes a bright red colour at the moment of contact with the drop of pyruvic acid. On gently warming the mixture, a liquid of a very deep blue colour is obtained, which spreads the same shade over the inner surface of the dish.

By the addition of water, or better still of concentrated alcohol, the resulting solution is of a transitory yellow colour.

2. *With the Sulphuric Acid Solution of α -Naphthol.*—At the ordinary temperature the reagent assumes a yellow colour at the moment of contact with the drop of acid.

If the liquid is very gently heated, it acquires a very deep orange shade, and when spread over the interior of the capsule it adheres firmly, varnishing it with the same colour.

By the addition of water no change of colour takes place; it is very stable.

Thus we see that these reactions not only serve to distinguish pyruvic acid from citric, tartaric, malic acid, &c., whose reactions with these reagents are very different; but they also furnish us with an easy method of distinguishing between α - and β -naphthols.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, April 19th, 1905.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

MR. B. PERROTT was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Joseph Bennett, North Adams, Mass., U.S.A.; Ralph Emerson De Lury, M.A., Manilla, Ontario, Canada; Robert Donald, M.A., B.Sc., M.R.C.S., L.R.C.P., D.P.H., 75, Clyde Street, Dunedin, N.Z.; Ernest Lyle Carman Forster, M.A., Brampton, Ontario, Canada.

Of the following papers, those marked * were read:—

*69. "Complex Nitrites of Bismuth." By WALTER CRAVEN BALL.

A very unstable, yellow, crystalline substance, probably $\text{Bi}(\text{NO}_2)_3 \cdot 2\text{NH}_4 \cdot \text{NO}_2 \cdot \text{NaNO}_2$, is precipitated by dissolving bismuth nitrate in sodium nitrite solution and pouring the resulting orange-coloured liquid into a saturated solution of ammonium nitrate at 0°. A more stable yellow compound, bismuth sodium ammonium nitrite, $\text{Bi}(\text{NO}_2)_3 \cdot 2\text{NH}_4 \cdot \text{NO}_2 \cdot \text{NaNO}_2$, which crystallises in octahedra, is obtained by dissolving bismuth nitrate in concentrated ammonium nitrate solution, and adding the resulting liquid to a saturated solution of sodium nitrite, cooled to 0°, and acidified with nitrous fumes.

A fairly stable, orange-yellow, bismuth potassium nitrite, $\text{Bi}(\text{NO}_2)_3 \cdot 3\text{KNO}_3 \cdot \text{H}_2\text{O}$, is formed when nitrous fumes are passed into bismuth hydroxide suspended in a concentrated solution of potassium nitrite. All these salts, which are decomposed by water, have a slight green fluorescence.

* The sulphuric acid solution of β -naphthol is a reddish yellow colour (orange).

† The sulphuric acid solution of α -naphthol is a gooseberry colour.

DISCUSSION.

Dr. L. F. GUTTMANN said that if the compounds described were analogous to the complex cobaltinitrites, it should be possible to prepare the corresponding barium or calcium double salt from the potassium compound, and asked whether the author had attempted to do so.

Mr. E. GRANT HOOPER expressed the opinion that precipitates produced as these substances were from saturated solutions might be expected to exhibit fair uniformity of composition if deposited under identical conditions, and that even close similarity of composition could not, in such circumstances, be deemed evidence that one was dealing with actual compounds and not merely mixed salts. He thought that especial care was necessary when the "compounds" were immediately decomposed either in the process of re-crystallisation or by any other treatment employed with the view of testing their individuality.

Mr. BALL, in reply, said that he had not succeeded in preparing pure specimens of other complex salts from the alkali double nitrites, mainly owing to their decomposition by solvents.

Mr. Hooper's view that these substances might be mixtures was rendered improbable by the fact that they had a well-defined crystalline form; moreover, they remained constant in composition even when prepared under varying conditions.

*70. "Experiments on the Synthesis of the Terpenes. Part II. Synthesis of Δ^3 -p-Menthenol(8), Δ^3 (8)-p-Menthadiene, p-Menthanol(8), Δ^8 (9)-p-Menthene, and p-Menthane." By WILLIAM HENRY PERKIN, jun., and SAMUEL SHROWDER PICKLES.

The authors deal with some hitherto unknown members of the terpene series which have been synthesised by employing Δ^1 tetrahydro- β -toluic acid instead of Δ^1 tetrahydro- β -toluic acid, and describe the synthesis of those compounds enumerated in the title.

*71. "Experiments on the Synthesis of the Terpenes. Part III. Synthesis of Aliphatic Compounds similar in Constitution to Terpineol and Dipentene." By WILLIAM HENRY PERKIN, jun., and SAMUEL SHROWDER PICKLES.

The authors describe the preparation of open chain compounds allied as closely as possible to the typical substances, terpineol and dipentene, in order to determine whether any great similarity in properties exists between such compounds and those members of the terpene group. The results indicate that probably the closed chain structure has a distinct influence on the properties of the terpenes and their derivatives.

*72. "Experiments on the Synthesis of the Terpenes. Part IV. Synthesis of Δ^3 -Normenthenol(8), Δ^3 (8)-Normenthadiene, Normenthanol(8), and Δ^8 (9)-Normenthene." By KOICHI MATSUBARA and WILLIAM HENRY PERKIN, jun.

In view of the close relation between terpenoid compounds and cymene, the authors have prepared a number of substances allied to those described in Part II. of this investigation, but differing from them in that they do not contain the methyl group.

73. "C-Phenyl-s-triazole." By GEORGE YOUNG.

C-Phenyl-s-triazole, $\text{N}-\text{NH} \begin{array}{c} \text{N} \\ \text{CPh} \cdot \text{N} \end{array} \text{CH}$, previously obtained

from 3-phenyl-1-methylhydroxy-1:2:4-triazole (*Trans.*, 1901, lxxix., 665), has now been prepared from C-phenylhydroxy-s-triazole (*Trans.*, 1900, lxxvii., 226); it melts at 119.5–120°. The silver nitrate derivative, $\text{C}_8\text{H}_6\text{N}_3\text{Ag} \cdot \text{AgNO}_3 \cdot 11\frac{1}{2}\text{H}_2\text{O}$, is obtained as a white precipitate; the platinumchloride, $(\text{C}_8\text{H}_7\text{N}_3)_2 \cdot \text{H}_2\text{PtCl}_6 \cdot 3\text{H}_2\text{O}$, when treated with water is converted into $(\text{C}_8\text{H}_{17}\text{N}_3)_2 \cdot \text{PtCl}_4 \cdot 3\text{H}_2\text{O}$. The acetyl derivative, $\text{C}_8\text{H}_6\text{N}_3 \cdot \text{C}_2\text{H}_3\text{O}$, melts at 90°; the carbamido-derivative, $\text{C}_8\text{H}_6\text{N}_3 \cdot \text{CO} \cdot \text{NH}_2$, melts at 117°.

74. "The Resolution of Inactive Glyceric Acid by Fermentation and by Brucine." By PERCY FARADAY FRANKLAND and EDWARD DONE.

Neuberg and Silbermann (*Ber.*, 1904, xxxvii., 339) state

that by the action of lime on *d*-glucuronic acid they have obtained a glyceric acid, of which the anhydrous barium salt in aqueous solution gives $[\alpha]_D +17.7^\circ$, whilst by the resolution of inactive glyceric acid with brucine the enantiomorphous barium salt, with rotation $[\alpha]_D -17.4^\circ$, was obtained.

These mutually corroborative results were calculated to throw the gravest doubt on the accuracy of the rotation, $[\alpha]_D 12^\circ -10.01^\circ$; given by P. Frankland and Appleyard (*Trans.*, 1893, lxiii., 299) for the barium salt of active glyceric acid obtained by the fermentation of inactive calcium glycerate with the *Bacillus ethaceticus* (P. Frankland and Frew, *Trans.*, 1891, lix., 81 and 96), whilst the optical purity of all the numerous other derivatives of the active fermentation glyceric acid were also thereby discredited.

The authors have in consequence re-investigated the barium salts obtainable from the fermentation acid, on the one hand, and from brucine resolution of the inactive acid on the other, with the result that both salts were found to have the same rotation, $[\alpha]_D 20^\circ -10.9^\circ$, which is thus entirely at variance with the figures of Neuberg and Silbermann. The clue to this unaccountable discrepancy was, however, wanting until quite recently, when Neuberg and Silbermann, in a foot-note at the end of a publication in the *Zeitschrift für Physiologische Chemie* (1903, xlv., 146), explained that the above values previously given by them for the rotation of the *d*- and *l*-glycerates of barium were erroneous through their having used a faulty polarimeter (displacement of the zero of the instrument).

The complete coincidence between the activity of the barium salt of the fermentation acid and of that of the acid obtained by resolution with brucine conclusively proves, not only the optical purity of each, but also the reliability of the material (the active calcium glycerate of P. Frankland and Frew) from which so many optically active derivatives have been prepared.

The fractionally higher specific rotation for the barium salt found by the authors, as compared with that given by P. Frankland and Appleyard, is doubtless to be accounted for by the circumstance that the salt has now been obtained in a more perfectly crystalline condition. The calcium salt, which had already previously been obtained in large crystals, exhibited the same rotation as before.

75. "Estimation of Potassium Permanganate in the presence of Potassium Persulphate." By JOHN ALBERT NEWTON FRIEND.

The author shows that small quantities of potassium permanganate may be correctly estimated iodometrically in the presence of potassium persulphate when the following precautions are observed:—

1. The solution should be diluted to at least 150 c.c. before addition of the iodide.

2. Very little more iodide should be added than is necessary to reduce the permanganate.

3. The acidity should be reduced to a minimum.

In this way, small quantities of permanganate may be estimated in the presence of as much as 0.08 gm. of persulphate.

Research Fund.

A meeting of the Research Fund Committee will be held in June next. Application for grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on or before Monday, June 5th, 1905.

ROYAL INSTITUTION.

Annual General Meeting, May 1st, 1905.

THE DUKE OF NORTHUMBERLAND, K.G., President, in the Chair.

THE Annual Report of the Committee of Visitors for the year 1904, testifying to the continued prosperity and efficient management of the Institution, was read and adopted, and the Report on the Davy Faraday Research

Laboratory of the Royal Institution, which accompanied it, was also read.

Seventy-one new Members were elected in 1904. Sixty-three Lectures and nineteen Evening Discourses were delivered in 1904. The books and pamphlets presented in 1904 amounted to about 267 volumes, making, with 721 volumes (including periodicals bound) purchased by the Managers, a total of 988 volumes added to the Library in the year.

Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committees of Managers and Visitors, and to the Professors for their valuable services to the Institution during the past year.

The following gentlemen were unanimously elected as Officers for the ensuing year:—

President—The Duke of Northumberland.

Treasurer—Sir James Crichton-Browne.

Secretary—Sir William Crookes.

Managers—Sir William de W. Abney, the Rt. Hon. Lord Alverstone, Henry E. Armstrong, Shelford Bidwell, Sir Alexander Binnie, The Hon. Sir Henry Burton Buckley, The Right Hon. Charles Scott Dickson, Francis Elgar, Maures Horner, Dr. Ludwig Mond, Sir Andrew Noble, Bart., The Right Hon. The Earl of Rosse, Sir Thomas Henry Sanderson, Alexander Siemens, and Silvanus P. Thompson.

Visitors—Dr. William Arthur Brailey, Dr. John Mitchell Bruce, Sir John George Craggs, Dr. James Mackenzie Davidson, Francis Fox, Robert Kaye Gray, Lord Greenock, Charles Edward Groves, A. Kirkham Lloyd, M.P., Sir Philip Magnus, Carl E. Melchers, Emile R. Merton, George Johnstone Stoney, John Jewell Vezey, and George Philip Willoughby.

NOTICES OF BOOKS.

The Analyst's Laboratory Companion. By ALFRED E. JOHNSON, B.Sc. (Lond.). Third Edition. London: J. and A. Churchill. 1904.

This handy little book has been enlarged and altered to such an extent in the third edition as to be hardly recognisable by those who have been accustomed to use the earlier editions, and it may be safely said that in every respect it has been improved. The author appears to have consulted the best authorities when collecting the data given in the various tables, with the result that his facts and figures may be accepted as the results of the most recent and accurate investigations; and the matter, as before, is well selected and put together in convenient form, so that probably no better book of the kind could be kept for reference in the laboratory. Special stress is laid upon the explanation and illustration of methods of solving the arithmetical problems occurring in analysis, abbreviated methods being fully discussed.

Marceli Nencki Opera Omnia. Gesammelte Arbeiten von Prof. M. Nencki. ("The Collected Works of Prof. M. Nencki"). Braunschweig: Friedrich Vieweg und Sohn. 1905.

In these two large volumes are collected for the first time all the late Prof. Nencki's papers. The work of collection was made peculiarly difficult owing to the great number of periodicals, in at least four different languages, in which the papers first appeared, and this adds proportionally to the value of the collection. The papers include a few by Nencki's pupils, describing researches undertaken at his instigation and under his immediate direction, and with the exception of one, which is now of historical interest only and is reproduced in the original Polish, are either in French or German. They are arranged chronologically, and deal with subjects belonging to pure organic chemistry, physiological chemistry, and bacteriology; the excellent scheme given at the beginning of the first volume, where

all the papers are tabulated according to the above division of their subject-matter, will be found of great use to the reader. In fact, these two volumes with their short biographical sketch, their systematic index, and chronological table of contents, form an excellent illustration of how a collection of this kind should be edited.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxi., No. 14, April 3, 1905.

Use of Hot and Cold Tubes in Chemical Reactions.—M. Berthelot.—The author's series of researches show clearly the exact effects of the instantaneous cooling of a gaseous mass. This mass is maintained at a constant temperature and then very rapidly transferred to a much lower temperature, also perfectly constant. The results tend to confirm the author's suppositions relative to the formation of certain gaseous bodies at high temperatures, and due to this influence alone.

Variation in the Band Spectrum of Carbon due to Pressure, and New Band Spectra of Carbon.—H. Deslandres and M. d'Azambuja.—The band spectra of carbon vary in the same manner as the negative group in air. They are, however, more difficult to examine, because of the slight intensity of the light and slight dispersion with the spectroscope. The positive bands also show analogous modifications, but as they have a much more complex structure they require more powerful apparatus, and will be examined in a future research. A new band is found with lines between λ 410 and λ 330.

Properties of Tungstic Anhydride as a Colouring Matter for Glass.—Albert Granger.—The good yellow colour of tungstic anhydride and its stability at temperatures used in the glass industry have led various authors to experiment on this substance. The present author finds that there are certain difficulties which all tend to render the anhydride more or less opaque. He is further investigating the conditions necessary for retaining its transparency in glasses and porcelains.

Preparation of Hydrosulphites.—M. Billy.—The author finds that sulphurous anhydride does not react on sodium in presence of a neutral solvent. In the presence, however, of absolute alcohol a reaction takes place. It apparently seems necessary to obtain the hydrosulphite for the sodium and the sulphurous anhydride to come together in presence of a reagent attacked by the metal. On trying to generalise this reaction, he finds that sulphurous anhydride reacts on magnesium also in presence of absolute alcohol, giving a hydrosulphite. The author's explanation is that the metal attacks the alcohol, forming a trace of alcoholate and hydride which react on the sulphurous anhydride, the hydrogen then reacting on a further portion of the metal.

Acetyl-lactic Acid.—V. Auger.—It is possible that Wislicenus prepared a very impure acetyl-lactic acid, but the properties of the pure product are very different from the acid prepared by Siegfried, who further investigated the properties of this substance. It is also possible that it represents a particular stereo-chemical polymer or isomer. It would be necessary in any case to find an advantageous method of preparation of this substance, because Siegfried seems never to have had more than minute quantities at a time.

Compounds of Chloro-aluminic Ferments with Hydrocarbides and Hydrochloric Acid.—G. Gustavson.—The author finds that chloro-aluminic

ferments, which are formed in the first place with evolution of heat when alcoholic chlorides are put in contact with benzene and aluminium chloride, have the remarkable property of uniting simultaneously with carbides and hydrochloric acid. Doubtless this property is allied very closely to the reactions of Friedel and Crafts; that is, with the transformation of alcoholic chlorides and benzene into aromatic carbides and hydrochloric acid gas.

Retrogradation of Artificial Starches.—E. Roux.—Already noticed.

Influence of the Ethylenic Function in an Active Molecule.—J. Minguin.—The increase in the rotatory power under the influence of the double liaison has been noticed by a number of investigators. The author also has previously shown that methylene camphor and ethylidene camphor have a rotatory power much superior to their corresponding saturated derivatives. He also found that the permanent deviations of the succinate, maleate, and fumarate of strychnine are different, and increase from succinate to fumarate. He now finds that the deviation given by the crotonate of strychnine is higher than that of butyrate, and proves that it is the same with the active ether salts of the same acids. His experiments are especially directed to the salts of amyl and bornyl.

MISCELLANEOUS.

The Society of Dyers and Colourists.—The Council of the Society have pleasure in announcing that funds have been placed at their disposal for distribution in the form of prizes for the solution of technical problems.

1. Prize of £20 for a satisfactory systematic tabulation of the reactions of dye-stuffs on the fibre, and a comprehensive scheme for their identification on dyed fabrics. The scheme should include the principal colouring matters dyed singly on all fibres for which they are employed. Competitors may adopt any method of classification they think desirable, but it is suggested that one or two reagents only be used as group tests, other reagents being subsequently applied for distinguishing the individual colours in a particular group.
2. Prize of £10 for a reliable method of distinguishing between unmercerised and mercerised cotton of various qualities, and for the estimation of the degree of mercerisation without reference to lustre.
3. Prize of £20 for a full investigation of the causes of the tendering of cotton dyed with sulphide blacks, and the best means of preventing such tendering.
4. Prize of £20 for a satisfactory standardisation of the strength and elasticity of cotton yarns of various qualities and twists in the grey and bleached conditions.
5. Prize of £20 for a full investigation of the average degree of tendering brought about in cotton yarn of various qualities by—(a) Cross dyeing with acid colours, (b) dyeing aniline black, and (c) various other dyeing processes, with the object of fixing standards for the trade.

The Hon. Secretary of the Society will be glad to communicate with anyone desiring to include further problems in the above list.—ERNEST T. HOLDSWORTH, Hon. Sec., Westholme, Great Horton, Bradford.

Second International Petroleum Congress.—An International Petroleum Congress will be held at Liège from June 26 to July 1, 1905, on the occasion of the Universal Exhibition. The Congress is under the patronage of the Belgium Government. The Minister of Foreign Affairs, M. Baron de Favereau, and the Minister of Industry and Labour, M. G. Francotte, have consented to act as honorary presidents. The Congress is organised with the collaboration of the permanent Commission of International

Petroleum Congresses, which has been instituted by the first Congress held in Paris in 1900. The Belgian Organising Committee is composed as follows:—

President—L. Dejardin, Chief Engineer of Mines, Director of the Ministry of Industry and Labour, and President of the Commission of Petroleum and Inflammable Substances.

Vice Presidents—(First Section) A. Habets, Professor at the Liège University; (Second Section) Fr. de Walque, Professor at the Louvain University; (Third Section) L. Gody, Professor at the Military and War Colleges; (Fourth Section) L. van Overstraeten, Inspector-General of Labour in the Ministry of Industry and Labour.

General Secretary—F. Petit, Delegate from the Permanent Committee of the Petroleum Congress, Brussels.

Secretary and Treasurer—Wm. Paul Legrande, Engineer, Brussels.

Members—Messrs. Aerts, Engineer and Manager of the Brussels Gas Works; Angenot, Professor of the Institute of Commerce, Antwerp; Aulit, Manufacturer, Brussels; Dekeyzer, Manufacturer, Brussels; Blazy, Manufacturer, Brussels; L. Lecocq, Chemical Engineer, Charleroi; Lohest, Professor of the Liège University; Mourlon, Director of the Belgium Geological Survey; Nicolas, Chemist of the State Railway Administration; Simonis, Assistant General Secretary of the Liège Exhibition; Waterkeyn, Manufacturer, Antwerp.

The General Programme will embrace four Sections:—First Section—Geology, Exploration, Exploitation; Second Section—Chemistry and Industrial Treatment; Third Section—Utilisation of Petroleum and its Derivatives; Fourth Section—Legislation.

Institute of Chemistry of Great Britain and Ireland.—*Pass List of the April Examinations.*—Of 6 Candidates who entered for the Intermediate Examination, 3 passed: J. D. Kettle, B.Sc. (Lond.), Elison A. Macadam, and R. Simmons. In the Final Examination for the Associateship (A.I.C.), of 7 examined in the branch of Mineral Chemistry, 3 passed: J. Alexander, B. O'Shaughnessy, Assoc.R.C.Sc. (Lond.), and E. Rhodes, B.Sc. (Vict.); of 5 in Organic Chemistry, 3 passed: S. J. M. Auld, Ph.D. (Würzburg), H. W. Goodwin, and E. Robison; and of 8 who entered in the branch of the Analysis of Food and Drugs and of Water, including an Examination in Therapeutics, Pharmacology, and Microscopy, the following 6 passed: J. H. Barnes, B.Sc. (Birm.), J. W. Brisbane, D. Gair, B.Sc. (Lond.), H. G. Harrison, B.A. (Cantab.), R. Park, and J. Race. One candidate passed an Examination for the Fellowship (F.I.C.): A. E. Brown, B.Sc. (Lond.). The Examiners in Chemistry were Mr. W. W. Fisher, M.A. (Oxon.), F.I.C., and Dr. G. G. Henderson, M.A., F.I.C. The Examination in Therapeutics, Pharmacology, and Microscopy was conducted by Dr. F. Gowland Hopkins, M.A., F.I.C.

Alcohol for Industrial Purposes.—**Complimentary Dinner to Mr. Thomas Tyrer.**—At a meeting of a Joint Committee representative of the Chemical Trade Section of the Chamber of Commerce, the Society of Chemical Industry, the Drug Club, the Society of Motor Manufacturers and Traders, the West India Committee, the Automobile Club, and others, held on April 5th, it was decided to arrange a Complimentary Dinner to Mr. Thomas Tyrer, to which the presence of representatives of branches of the chemical, pharmaceutical, and other trades concerned should be invited. Mr. Tyrer has for years past persistently followed up the question of untaxed alcohol for manufacturing purposes, and it was largely due to his efforts that the Chancellor of the Exchequer, in October last, appointed the Departmental Committee to inquire into the use of Duty Free Alcohol for industrial purposes, and of which Committee Mr. Tyrer himself was a member. Mr. Tyrer was for many years the Chairman of the

Chemical Trade Section of the London Chamber of Commerce, and is now a member of its Council, and he has also held high office in the Society of Chemical Industry, in all of which positions he has worked in an arduous and unselfish manner, and it has been felt that some public appreciation of his endeavours on behalf of the trades specially concerned should be accorded to him. On the occasion of the Dinner to Mr. Tyrer (May 25th) it is proposed to make a presentation to that gentleman, in the form of an Illuminated Address and a piece of Plate suitably inscribed, as a memento of the occasion, and a permanent record of the gratitude and respect which is felt by members of the Chemical and Drug Trades to Mr. Tyrer for his active work on their behalf extending over a long period of years.

MEETINGS FOR THE WEEK.

MONDAY, 8th.—Royal Institution, 5. General Monthly Meeting.
— Society of Arts, 8. (Cantor Lectures). "Some Aspects of Ancient and Modern Embroidery," by Alan S. Cole, C.B.
TUESDAY, 9th.—Royal Institution, 5. "The Study of Extinct Animals," by Prof. L. C. Miall, F.R.S., &c.
WEDNESDAY, 10th.—Society of Arts, 8. "The Native Races of the Unknown Heart of Central Africa," by The Viscount Mountmorres.
THURSDAY, 11th.—Royal Institution, 5. "Flame," by Prof. Sir James Dewar, F.R.S., &c.
— Society of Arts, 4.30. "The Manufactures of Greater Britain—India," by H. J. Tozer, M.A.
FRIDAY, 12th.—Royal Institution, 9. "Pressure due to Radiation," by Prof. Ernest Fox Nichols.
— Physical, 8. "Simple Method of Determining the Radiation Constant," by Dr. A. D. Denning. "Bolometer for the Absolute Measurement of Radiation," by Prof. H. L. Callendar. "The Resistance of a Conductor the Measure of the Current flowing through it," by W. A. Price.
SATURDAY, 13th.—Royal Institution, 3. "Moulds and Mouldiness," by Prof. Marshall Ward, F.R.S., &c.

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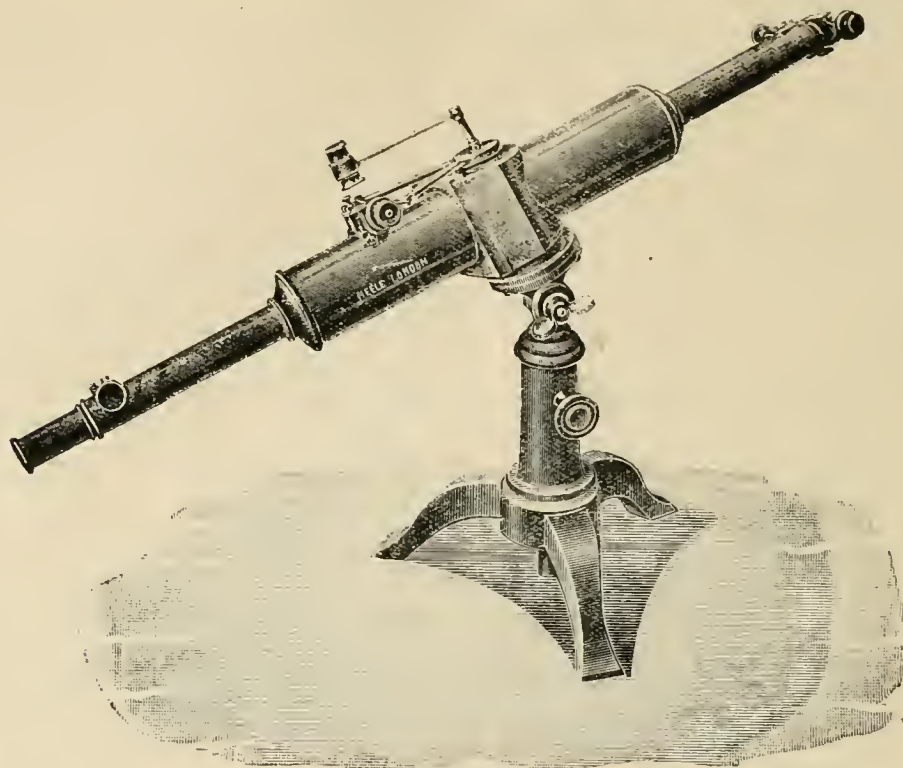
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THE CHEMICAL NEWS.

VOL. XCI., No. 2372.

ON THE ESTIMATION OF FREE ACID AND ITS RELATION TO TOTAL ACIDITY IN SUPERPHOSPHATE.

By J. OSTERSETER, F.I.C., F.C.S.

IN an article, "Note on Free Acid in Superphosphate," published in 1902 (CHEMICAL NEWS, vol. lxxxv., 195), the writer referred to the use of alizarin sulphonic acid as a suitable indicator for the technical estimation of free acid forming an integral part of what may be termed the total acidity in superphosphate. The latter is indicated by methyl-orange with NaHO, and includes, in addition to free acid, more or less considerable quantities of combined phosphoric acid, varying frequently according to the amount of Fe and Al contained by the different raw materials used in the manufacture of superphosphate. The *modus operandi* may be described as follows, viz. :—

Dissolve 10 grms. superphosphate in 400 c.c. water in a 500 c.c. flask, shake for the usual time, add 4 c.c. of a solution containing 2½ grms. sodium salt of alizarin sulphonic acid in 500 c.c. water; complete the volume with water in the first named 500 c.c. flask, and filter; titrate 50 c.c. or 10 grm. of the substance with N/2 NaHO to the transition between yellow and brown, comparing the same with a similar volume of the original coloured liquid in order better to observe the intermediate tint, showing a distinct tinge of brown, which is generally succeeded by partial dissociation of the solution. The result is calculated as free acid, and compared with that of total acidity determined in the usual way at the point of neutrality.

North Wall, Dublin, April 26, 1905.

THE DETERMINATION OF CARBONIC ACID IN THE PRESENCE OF CHLORINE, AND ESPECIALLY ELECTROLYTIC CHLORINE.

By MAX SCHLÖTTER.

C. OFFERHAUS has described three analytical methods which all depend on the absorption of the carbonic acid and the chlorine by a solution of soda. The chlorine is then titrated by means of a solution of iodide of potassium, estimating the iodine liberated; and the carbonic acid by means of hydrochloric or oxalic acids.

This process has the drawback that we have to use volumetric and gasometric methods simultaneously, which complicates the calculation of the results. In short, these methods do not appear to me to possess the simplicity required by the practical chemist.

The very active properties of chlorine may lead to various determinations by the gasometric method. In this manner Winkler made use of its property of oxidising the solutions of ferrous salts into ferric salts. We can also use a solution of cuprous chloride.

For the absorption of chlorine I make use of hydrazine or its salts.

As I have already shown (*Zeit. Anorg. Chem.*, vol. xxxvii., p. 164), the halogens act on hydrazine according to the equation, $N_2H_4 + 2Cl_2 = 4HCl + N_2$; that is to say, one volume of nitrogen corresponds to two volumes of chlorine.

The operation is very simple. We introduce into a

Bunte burette 100 c.c. of gas, water is used to establish the correct level; the use of 20 to 25 c.c. of this liquid does not cause any appreciable error.

Then we place in the burette a solution of sulphate of hydrazine, shake for some minutes, and add a further quantity of sulphate of hydrazine. The reaction once finished, we read off the diminution of volume; by doubling the number found we have the volume of chlorine.

Before determining the carbonic acid it is as well to eliminate as much as possible of the hydrazine. R. Stolle (*Journ. Prakt. Chem.*, 1902, p. 322) has shown that solutions of hydrazine decompose easily in the presence of carbonates and bicarbonates.

To compare this method with that of M. Offerhaus, I prepared, like him, mixtures of air, chlorine, and carbonic acid, and I made the analyses both by his method and by my own; the following are the results obtained :—

No.	Method of Offerhaus.		Hydrazine method.	
	Cl. Vol. per cent.	CO ₂ . Vol. per cent.	Cl. Vol. per cent.	CO ₂ . Vol. per cent.
1.	42·86	9·5	42·8	9·6
2.	23·6	13·0	24·0	13·2
3.	33·8	58·2	33·6	58·0

We see from the above figures that the method in question is perfectly applicable, and it has the advantages of simplicity and rapidity over that of M. Offerhaus.—*Zeitschrift für Angewandte Chemie*, 1904, p. 301.

RAPID METHOD FOR THE ESTIMATION OF THE HALOGENS IN ORGANIC BODIES BY MEANS OF PEROXIDE OF SODIUM.

By P. PRINGSHEIM.

THE estimation of the halogens in organic compounds, without having recourse to the use of sealed tubes necessitating the use of Carius's method, has been recently the subject of a research by M. Dittrich (*Ber.*, vol. xxxvi., p. 3285).

I have attempted to solve this problem by the use of peroxide of sodium, and I have succeeded in establishing a method of estimation, possessing all the necessary qualifications of accuracy, rapidity, and cheapness, besides being capable of very numerous applications. The organic matter to be examined is mixed with a suitable proportion of peroxide of sodium; substances containing 75 per cent and more of total carbon + hydrogen requires 18 times their weight of peroxide of sodium; those containing from 50 to 75 per cent of these same elements must have 16 times their weight of the reagent. If we have to deal with a substance containing from 25 to 50 per cent of carbon and hydrogen, we must add to it half its weight of some other substance rich in carbon and hydrogen, such as sugar, naphthalene, &c., before mixing it with the 16 parts of peroxide. Finally, in those rare cases of a substance containing a still less quantity of combustible elements, we add its own weight of sugar, for example, and 18 parts of Na₂O₂.

The estimation is effected in the following manner :—

We weigh out about 2 decigrams. of the substance, and place it in a small steel crucible of cylindrical shape, with the calculated quantity of Na₂O₂. The crucible must only be two-thirds of its height full; this is put in a porcelain crucible, in which a little cold water is carefully placed, so that the steel crucible stands out by 1 or 2 c.m. This latter crucible is covered with its own cover, in which is a hole through which an iron wire heated to redness can be introduced with the object of starting the combustion. As soon as the combustion is completed the whole is plunged into the water, the porcelain crucible covered with a watch-glass, and heated gently until the whole mass is dissolved. This point is recognised when no more bubbles of oxygen

are given off, and when there are no more particles of carbon which have escaped combustion. The steel crucible is then removed and washed carefully; the solution is filtered, and treated with an excess of sulphurous acid. This acid is to neutralise the alkaline liquid, and to reduce the oxidised products (bromic acid, iodic acid, &c.), resulting from a too energetic oxidation to the state of hydracids (hydrobromic acid, hydriodic acid, &c.). We then acidulate with nitric acid, and precipitate the solution, which should occupy about 500 c.c., with nitrate of silver; the nitric acid keeps the sulphite of silver in solution. The whole is kept on the water-bath for some time so as to collect the precipitate, which is filtered, washed, and weighed in the ordinary manner.

Iodoform, CHI_3 .—Substance = 0.1345 grm., AgI = 0.2407 grm., I = 0.1292 grm. I per cent calculated = 96.62; found = 96.69.

p-Dibromobenzol, $\text{C}_6\text{H}_4\text{Br}_2$.—Substance = 0.4875 grm., AgBr = 0.7779 grm., Br = 0.3310 grm. Br per cent calculated = 67.79; found = 67.76.

Dibromosuccinic Acid, $\text{C}_2\text{H}_4\text{O}_4\text{Br}_2$.—Substance = 0.3479 grm., AgBr = 0.4740 grm., Br = 0.2017 grm. Br per cent calculated = 57.97; found = 57.98.

Chloranile, $\text{C}_6\text{O}_2\text{Cl}_2$.—Substance = 0.1136 grm., AgCl = 0.2645 grm., Cl = 0.0654 grm. Cl per cent calculated = 57.73; found = 57.57.

All the substances analysed up to the present have given me good results, although they belong both to the fatty and the aromatic series, and contain the most various groups; therefore I consider that this is a general method. I propose to extend its application to other elements, especially to nitrogen; the method for the estimation of sulphur proposed by F. von Konek (*Zeit. Angew. Chem.*, xvi., p. 516), and in which Parr's calorimetric bomb (*Journ. Am. Chem. Soc.*, xxii., p. 664) is used, can be simplified by the use of the steel crucible.—*Berichte*, vol. xxxvi., p. 4244.

A REACTION OF THE COMPOUNDS OF RHODIUM OF USE IN CHEMICAL ANALYSIS.

By Dr. EUGENIO PINERUA ALVAREZ,
Professor of General Chemistry of the Faculty of Sciences, Madrid.

In summarising the experimental analytical research on the rhodium compounds, one notices an absence of any sensitive characteristic reaction which serves to distinguish this metal easily and decisively from all the others of the same group.

The production of sulphides, investigated in detail by Leidié, that of the purple, pink, and yellow xanthorhodic compounds discovered by Jørgensen, Blomstrand, Gibbs and Genthe, Topsoë, &c.; those of the chlorides and other halogen compounds discovered by Felleberg, Seubert, Kobée, &c.; those of the cyanide compounds investigated from an analytical point of view by Martius, Rose, Finkener, Demarçay, and many other chemists, do not furnish us with any ready means of recognising these metallic compounds.

The Demarçay reaction, the one most used in analysis, is very far from possessing the advantageous qualities assigned to it.

The blue liquid which, according to Claus, is produced by obtaining the green precipitate of orthorhodic hydrate, $\text{Rh}(\text{OH})_4$, by oxidising indirectly with chlorine or a hypochlorite, an alkaline solution of a rhodium salt, may be characteristic of great analytical importance by acting in the manner which we are about to describe, and which we have employed in teaching the reactions of these compounds in the laboratory.

To a dilute aqueous solution of any soluble salt of rhodium, as, for example, sodium chlor-rhodate,

$\text{RhCl}_3 \cdot 3\text{ClNa} = \text{RhCl}_6\text{Na}_3$,* an excess of soda (NaOH) is added in the cold in order to obtain an alkaline solution of hydrated sesquihydrate of rhodium, $\text{Rh}(\text{OH})_3 \cdot \text{H}_2\text{O}$,† and this liquid is then exposed to the gaseous mixture produced by the action in the cold of concentrated hydrochloric acid upon potassium chlorate, using a test-tube fitted with another narrower tube for conducting the gas, the end of which is introduced into the solution.

We notice the following phenomena:—At first the very dilute and almost colourless alkaline solution of sodium chlor-rhodate acquires a reddish yellow colour, which changes immediately to red; this red colouration rapidly becomes very intense until a moment arrives—if the current of chlorinating gases continues to act—when the liquid darkens, and begins to become cloudy with the formation of a faint green precipitate, which finally dissolves, giving rise to a liquid of a beautiful blue colour, in appearance very like those of ammoniacal copper solutions. The soluble compound, which in solution gives this blue colour to the liquid, is the sodium per-rhodate of Claus, RhO_4Na_2 .

On acting upon this liquid with a fresh solution of sulphurous acid gas, it immediately loses its blue colour, and acquires a light yellow colouration, due to the rhodic sulphate which is produced.

The peroxide and persulphate of sodium also decolourise the liquid with copious effervescence, caused by the liberation of oxygen from the peroxidised alkalis and from the per-rhodate.

Chloroform, anhydrous ether, and pure benzene do not dissolve this blue compound of rhodium.

Pure aniline acquires a red colour (due to the partial reduction of the per-rhodic compound), and the liquid loses its colour.

On summing up the foregoing, we see that the production of per-rhodic acid, or of per-rhodate of sodium, by the method we have described, furnishes us with an easy sensitive characteristic means of distinguishing rhodium from all the other metals of the same group.

LOW TEMPERATURE INVESTIGATIONS.‡

By Professor Sir JAMES DEWAR, D.Sc., F.R.S., &c.

In the Friday Evening Discourse delivered in the year 1896, entitled "New Researches on Liquid Air (*Proc. Roy. Inst.*), it was shown that seven substances, having very different coefficients of expansion, viz., cadmium, lead, copper, silver, calc spar, rock crystal, silver iodide, all gave the same density for liquid oxygen, when used to determine the weight displacement in the liquid, provided the correcting factor used in each case was the calculated mean coefficient of cubical expansion found by extending the values of Fizeau to low temperatures. The fact of the uniformity in the resulting oxygen density proved that the parabolic law of Fizeau may safely be used for extrapolation at low temperatures as far as the boiling point of air, especially in the case of the metals.

The determination of the densities of substances at the boiling point of oxygen—and hence of their mean coefficients of expansion between that temperature and ordinary temperatures—opens out a very large field of investigation, from which, if a sufficiently large number of observations were available, valuable deductions might be drawn. On account, however, of the expense and trouble of producing quantities of liquid oxygen, its use for this purpose is not likely to become general, although, when available, it is the easiest body to use in conducting such experiments.

* We obtained the chlor-rhodate of soda by bringing to a red heat a mixture of powdered commercial rhodium and four times its weight of fused sodium chloride, and introducing the mixture into a Jena glass tube traversed by a current of dry chlorine.

† The formula $\text{Rh}(\text{OH})_3 \cdot \text{H}_2\text{O}$ is equal to $\frac{1}{2}\text{Rh}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$, called hydrated sesquioxide of rhodium.

‡ A Lecture delivered at the Royal Institution of Great Britain, January 16, 1903.

especially when the vacuum vessel containing it is immersed in a larger vessel containing the same fluid or well evaporated air. The ease with which liquid air can now be obtained in many laboratories suggests that its application to work of this kind would be a convenience. The use of a mixture of varying composition and density like liquid air necessitates a determination of its density with accuracy and rapidly before and during the course of the experiments. For this purpose, liquid air that had been allowed to evaporate for twenty-four hours in advance was used in large silver-coated vacuum vessels of some 3 litres capacity. In order to ascertain the density of the liquid, a polished silver ball, which had been weighed once for all in liquid oxygen, was weighed in the sample of liquid air, and from the relative weights thus found the density of the liquid air could be approximately determined, that of liquid oxygen being 1.137. To prevent any disturbing ebullition in the liquid-air flask in which the weighings took place, and to reduce the rate of its evaporation to a minimum during the course of an experiment, the substance to be used was previously cooled in a supplementary vessel containing liquid air, and then transferred to the large flask. Substances like solid carbonic acid and ice were weighed in the cool gaseous air of the vacuum vessel, and their weights subsequently corrected for buoyancy. The temperatures of the densest and lightest samples of liquid air were ascertained by the hydrogen thermometer, and that of the others deduced by graphic interpolation. As the entire range of temperature through which the bodies were cooled amounted to about 200°, a degree or two up or down has no real influence on the results; the extreme range of temperature in the air samples was from 83.8° to 86.1° absolute.

Salts were employed in the form of compressed blocks. The salt, previously reduced to a fine powder, was moistened with water and compressed in a cylindrical steel mould under great hydraulic pressure. During compression the saturated salt solution drained away, and finally a cylindrical block of some 50 grms. of the salt was obtained free from porosity and hard enough to allow its surface to be polished. In this form salts and other materials similarly treated are especially adapted for accurate specific gravity determinations. After such treatment it was found that all the mechanically attached water was got rid of in the case of hydrated salts, and also in such as did not combine with water. In order to get cylindrical blocks of the salts showing no porosity, the presence of water, or rather the saturated salt solution, was found to be essential during the application of pressure. In the same way it was found to be an advantage in compressing such a substance as solid carbonic acid, to moisten it with a fluid like ether before applying the hydraulic pressure.

Recalling the work of Playfair and Joule ("Researches on Atomic Volume and Specific Gravity," *Chem. Soc. Journ.*, vol. i., 121), which originated in a suggestion of Dalton's that the volume of a hydrated salt in solution was simply the volume of the water of crystallisation as ice, some hydrated salts were selected, as well as some other bodies whose coefficients of expansion they had determined. Substances of special interest included in the list, were ice, mercury, sulphur, iodine, and solid carbonic acid, the latter being particularly important as an example of a solidified gas.

The specific gravity of the actual portion of the substance weighed in the liquid air was, with one or two exceptions, determined also at the temperature of the laboratory, about 17° C. From the two sets of observations the value of the mean coefficient of cubical expansion between 17° C. and the temperature of liquid air, was calculated, and whenever the expression coefficient of expansion is used, the volume coefficient is meant.

Ice at Low Temperatures.

The actual density at the temperature of liquid air of pieces of ice cut from large blocks, gave the value 0.92999.

The density at 0° being 0.91599, this gives for the mean cubical coefficient 0.0008099.

We may take 0.0007551 as the mean coefficient of expansion of ice between 0° and -20° C. Thus the mean coefficient of expansion between 0° and -188° C. is about half of that between 0° and -20° C. The mean coefficient of expansion of water in passing from 4° to -10° C., is -0.000362, and from 4° to 40° C. it is 0.0002155. Hence the mean coefficient of expansion of ice between 0° and -188° C. is about one-fourth of that of water between 0° and 10° C., and half of that between 4° and 100° C.

If the densities of ice at still lower temperatures could be determined, the values of the coefficient of expansion thence deduced would, we have every reason to believe, be less than the value given above. We shall therefore not be overstraining the case if we use the value just found to determine an upper limit to the density of ice at the absolute zero. The result is 0.9368, corresponding to a specific volume 1.0675. Now the density of water at the boiling-point is 0.9586 (corresponding to the specific volume 1.0432), so that ice can never be cooled low enough to reduce its volume to that of the liquid taken at any temperature under one atmosphere pressure. In other words, ice molecules can never be so closely packed by thermal contraction as the water molecules are in the ordinary liquid condition, or the volume of ice at or near the absolute zero is not the minimum volume of the water molecules. It has been observed by Professor Poynting ("Change of State, Solid, Liquid," *Phil. Mag.*, 1881) that if we suppose water could be cooled without freezing, then taking Brunner's coefficient for ice, and Hallstrom's formula for the volume of water at temperatures below 4° C., it follows that ice and water would have the same specific volume at some temperature between -120° and -130° C. Applying then the ordinary thermodynamic relation, no change of state between ice and water could be brought about below this temperature. Clausius has shown that the latent heat of fusion of ice must be lowered with the temperature of fusion some 0.603 of a unit per degree. If such a decrement is assumed to be constant, then about -130° C. the latent heat of fluidity would vanish. Thus under a pressure of about 16,000 atmospheres at this low temperature there ought theoretically, if the extrapolation pressure were legitimate, to be no distinction between the solid and liquid forms of water. At temperatures below this limit no amount of pressure would transform ice into water.

In inferring at what temperature this kind of critical point of the possible transition of ice into water takes place, no consideration of the change in the specific heats of ice and water under the greatly increased pressures have been included. If this is done, then it appears that ice under 50 tons and a corresponding temperature of about -50° C., would be all transformed into water, so that no lower temperature could be reached by any forced transition. All such speculations based on imperfect data are cleared away by the important experiment made by Tamman, who has shown that ice under a pressure of 20 to 30 tons on the square inch and a temperature of -22° or -23° becomes transformed into a new variety of ice, which under the specified conditions of temperature and pressure is denser than water. This new ice has a density greater than water, viz., 1.11, so that no amount of pressure on ice below the temperature of -23°, can cause any transition. All the theoretical anticipations of the relations of ice and water at very low temperatures and high pressures have been entirely falsified by the results of Tamman.

Ice near its melting point can easily be squeezed into the form of wire when forced by hydraulic pressure from a steel cylinder having a small aperture in the bottom. If the temperature of the ice is lowered to -80 C. by embedding the steel cylinder and plunger in solid carbonic acid under a pressure of 50 tons, the flow still takes place. The ice wire was now made up of what looked like a set of disc-like scales, which contrasted strongly in appearance with the transparent clear ice wire got when the experi-

Cooled Rubber Films.

One of the most interesting illustrations of the increased strength and elasticity of a body at the lowest temperatures is to take the case of a very thin transparent film of india-rubber. The film is stretched over one end of a short glass tube about the diameter of a good wide test-tube, the other end being contracted and sealed on to a long narrow tube that, after being bent twice at right angles, has still one limb more than 30 in. long. The film end of the test-tube can now be immersed in liquid air, while the end of the long tube is placed in a vessel containing mercury in order to observe the diminution of pressure in inches of mercury. When the whole test-tube part covered by the film is cooled in liquid air, a diminution of from 9 to 10 in. of mercury may be observed. Under such conditions the film is perfectly tight, provided it has been tied on to the glass after a little coating of melted rubber has been applied to the surface. No liquid oxygen seems able to diffuse through the film, which is indeed remarkable considering the rapidity with which gaseous oxygen is known to pass. But the most remarkable fact of all is that the liquid air surrounding the film may be replaced by a vessel containing liquid hydrogen, which instantly solidifies all the air in the film-enclosed space, giving almost a perfect vacuum, as proved by the mercury column rising to the height of the barometer at the time, and yet the film stands the pressure when cooled to $-252^{\circ}\text{C}.$, and further resists the passage of hydrogen by molecular diffusion. In the cooled state such films, when struck with a cork hammer, give out a clear metallic ring, and if the striking is continued during the heating up of the film, a complete gamut of notes is produced from the varying elasticity. After returning to the ordinary temperature the film recovers all its ordinary properties.

Molecular Volumes at the Zero of Temperature.

Theoretical formulæ enable an estimate to be formed of the volume of the gram-molecule of many bodies at the zero of temperature. The direct experimental method is to ascertain the densities of bodies as near the zero of temperature as possible. By means of the use of liquid hydrogen as a cooling agent instead of liquid air densities might be determined within 20° of the zero. In the meantime the limiting densities of oxygen, nitrogen, and hydrogen have been found, together with the coefficients of expansion about their boiling points. The approximate results are given in the following table:—

TABLE II.

	Density at boiling point.	Density at 62.5°Ab.	Density at 20°Ab.	Density at 15°Ab.	Coefficient of expansion.
Oxygen ..	1.12	1.24	1.42	—	0.004
Nitrogen .	0.80	0.88	1.03	—	0.006
Hydrogen	0.07	—	—	0.076	0.013

Thus solid oxygen and nitrogen are respectively some 18 and 14 times denser than solid hydrogen, while the expansion coefficients of oxygen, nitrogen, and hydrogen are roughly in the ratio of 1, 1.4, and 3. With these values the molecular volumes at the absolute zero can be inferred, if we assume the general application of what is called the Matthias Law of the rectilinear semi-diameter. The values which result for oxygen, nitrogen, and hydrogen are respectively 21.2, 25.5, 24.2. The volume in c.c. of the gram-molecule of these three elements does not differ much from the mean value 23.6 c.c. The experiments already described on the density of ice and solid carbonic acid, about 90 absolute, enables an approximate estimate to be made of their zero-volumes, which results in the values of 19.2 for the ice molecule and 25.7 for the carbonic acid one. From these values, along with the molecular volumes given above for solid hydrogen and oxygen, we can ascertain the volume change that would result in the formation of the compound molecules of ice and solid carbonic acid—provided they could be formed by an

imaginary combination taking place, at the zero of the solid hydrogen and oxygen on the one hand, and the solid oxygen and carbon on the other. Thus it appears that 100 volumes of mixed hydrogen and oxygen in the solid state would after combination produce 55.2 volumes of ice, or the contraction would amount to 45 per cent of the initial volume of the mixture. This value is of the order of magnitude of the contraction which results from the combination of oxygen (solid) with metallic bodies like lithium and sodium, which is about 60 per cent. On the other hand, the production of solid carbonic acid from the diamond or graphite and solid oxygen, would in the former case involve an expansion of 41 per cent, while in the latter the contraction would not exceed some 3 per cent. Such considerations confirm the view that what we call the molecular volume at zero is not the real volume of the molecules, but includes a considerable amount of unoccupied free space.

TWELFTH ANNUAL REPORT

OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1904.*

By F. W. CLARKE.

THE year 1904 has been notably prolific in determinations of atomic weight, and the new data with regard to rubidium, glucinum, indium, and tungsten are of more than ordinary value. Most significant, however, is the work upon nitrogen and iodine, which tends to strengthen the growing impression that the more fundamental atomic weights need to be carefully revised.

Richards and Wells, in an oral communication before the American Chemical Society and the American Association for the Advancement of Science, have shown that the accepted values for sodium and chlorine are inexact, but the details of their research are as yet unpublished. Iodine has been corrected to the extent of a tenth of a unit, and the value 14.04 for nitrogen is seriously questioned. If we regard the hydrogen-oxygen ratios as fixed, the atomic weights which need immediate attention are those of silver, sodium, potassium, chlorine, bromine, iodine, nitrogen, carbon, and sulphur. These in great measure, but not absolutely, hinge upon the value assigned to silver, and that, in turn, depends upon the analyses of chlorates, bromates, and iodates. The atomic weight of silver, therefore, should be carefully scrutinised. Some of the desired revision is already under way in the hands of well-known investigators, but a large amount of exact work still remains to be done. A summary of the determinations published in 1904 is given below.

Hydrogen, Oxygen, Carbon, and Sulphur.

The new data relative to the atomic weights of these elements consist of determinations of gaseous densities, or of calculations based upon former measurements. Lord Rayleigh, for example, has studied, the compressibility of oxygen, hydrogen, nitrogen, and carbonic oxide, and compared their densities at atmospheric pressure and under conditions of great rarefaction (*Proc. Roy. Soc.*, lxxiii., 153; *CHEMICAL NEWS*, lxxxix., 86). In the latter case the best agreement with Avogadro's law is to be expected. Leaving nitrogen to be considered separately, the following values are given for the densities of H and CO, as compared with O = 16.

	Atmospheric pressure.	Very small pressure.
H	1.0075	1.0088
CO	14.000	14.003

From the last figure given, the atomic weight of carbon becomes 12.006. At low pressures, if H = 1, O = 15.860.

Guye and Mallet (*Comptes Rendus*, cxxxviii., 1034) have re-calculated Morley's data for the densities of hydrogen

* From the *Journal of the American Chemical Society*, xxvii., No. 3.

and oxygen, and find the ratio to be 1 : 15·8787. In a later paper (*Comptes Rendus*, cxxxviii., 1213) Guye computes the atomic weights of H and O from Morley's figures, and those of N and C from Rayleigh's work on N and CO. When O = 16, H = 1·00765 and C = 12·003. Jaquero and Pintza find the weight of 1 litre of oxygen at 0°, 760 m.m., and at sea-level in latitude 45°, to be 1·4292 grms. (*Comptes Rendus*, cxxxix., 129). This figure is the mean of five determinations. From the density of sulphur dioxide at different pressures they compute S = 32·01 when O = 16.

Nitrogen.

Lord Rayleigh, in the paper previously cited, finds the density of N at atmospheric pressure to be 1·4003, and at very low pressures 1·4009. Guye's calculations lead to the figure 1·4004.

Guye and Bogdan have re-determined the atomic weight of nitrogen by an entirely new method (*Comptes Rendus*, cxxxviii., 1494). A fine spiral of iron wire was burned in an atmosphere of nitrous oxide, the gas and iron both having been weighed. The iron oxide thus produced was also weighed, and from these data the atomic weight in question was calculated. The results were as follows when O = 16 :—

Weight N ₂ O.	Weight O.	Atomic weight N.
1·1670	0·4242	14·009
0·9498	0·3453	14·005
0·8652	0·3145	14·008
1·2247	0·4455	13·992
1·4202	0·5159	14·023
Mean		14·007

In what was evidently a continuation of the foregoing research, Jaquero and Bogdan studied nitrous oxide volumetrically (*Comptes Rendus*, cxxxix., 49). Iron wire was burned in the gas, and from the change in volume, by a method which is not explained in detail, they found N = 14·019. Still more recently, Guye and Pintza have re-determined the density of nitrous oxide (*Comptes Rendus*, cxxxix., 677). The weight of 1 litre, under normal conditions, was found to be as follows :—

1·97789
1·97774
1·97803

Mean .. 1·97788

On the supposition that carbon dioxide is comparable with nitrous oxide—that is, that the two gases are in corresponding states, the authors arrive at the atomic weight of nitrogen. The weight of CO₂, as the mean of Leduc's and Rayleigh's measurements, is 1·97693. Hence, 1·97693 : 1·97788 :: 44·005 : x, x = 44·026, and N = 14·013.

Although the new determinations of the atomic weight of nitrogen are by no means final and unimpeachable, they are remarkably concordant, and lead to the suspicion that the commonly accepted value, 14·04, is too high. Richards (*Proc. Am. Phil. Soc.*, xliii., 116), from a careful criticism of all former determinations, concluded that the true figure was not lower than 14·02 nor above 14·04, but this new work was not included in his discussion. Still lower values were obtained by Miss Aston from analyses of lithium, sodium, potassium, strontium, barium, and silver trinitrides, and ranged from 13·86 to 13·96, or 13·903 as the mean of eighteen determinations. This work, cited by Ramsay (*Gesellschaft Deutscher Naturforscher und Aerzte*, Meeting of 1903), at whose suggestion it was done, has not been published in detail, and cannot therefore be intelligently discussed. Ramsay, however, does not regard the results as conclusive. Evidently the atomic weight of nitrogen needs to be thoroughly re-investigated.

Iodine.

Two important researches upon the atomic weight of iodine have appeared during the year. That of Baxter was

the first one to be published in complete form (*Proc. Amer. Acad.*, xl., 419; *Journ. Am. Chem. Soc.*, xxvi., 1577), although it was preceded by a preliminary notice of the other investigation.

Baxter employed several methods of determination in which all the material used was scrupulously purified and all weights were reduced to a vacuum. Calculations were based upon O = 16, Ag = 107·93, and Cl = 35·467. The last value was recently announced by Richards and Wells, but the details which establish it are as yet unpublished. First, silver was converted into silver iodide. The metal was dissolved in nitric acid and precipitated by ammonium iodide in presence of an excess of ammonia. Two series of determinations were made, with the results given below :—

PRELIMINARY SERIES.

Weight Ag.	Weight AgI.	Atomic weight I.
5·23123	11·35331	126·970
3·57039	7·77033	126·961
4·60798	10·02804	126·951
4·52467	9·84822	126·986
4·66256	10·14591	126·930
Mean		126·960

FINAL SERIES.

Weight Ag.	Weight I.	Atomic weight I.
4·77244	10·38698	126·975
4·82882	10·50981	126·977
4·04262	8·79755	126·947
1·64711	3·58515	126·994
4·86054	10·57318	126·972
4·83482	10·52241	126·967
4·97120	10·81800	126·940
3·53858	7·70136	126·969
3·89693	8·48187	126·985
5·33031	11·60111	126·973
5·08748	11·07259	126·973
Mean		126·979

The seventh determination in the final series is rejected by Baxter, the mean value then becoming 126·973.

In the next series of experiments the ratio of silver to iodine was determined directly. Weighed quantities of iodine were converted into hydriodic acid by solution in sulphurous acid, then neutralised with ammonia, and titrated with a known amount of silver.

Weight Ag.	Weight I.	Atomic weight I.
5·54444	6·52288	126·977
6·27838	7·38647	126·979
4·57992	5·38814	126·976
Mean		126·977

Finally, the ratio of silver chloride to silver iodide was determined by heating the latter, in quartz crucibles, in a current of chlorine. In two experiments the iodide was first transformed into bromide and then heated in chlorine. The data are as follows :—

Weight AgI.	Weight AgCl.	Atomic weight I.
9·26860	5·65787	126·980
6·72061	4·10258	126·975
11·31825	6·90910	126·978
10·07029	6·74753	126·970
13·65457	8·33535	126·975
17·35528	10·59454	126·974
Mean		126·975

The mean of all three ratios is I = 126·975—a confirmation of the conclusions previously reached by Ladenburg. A continuation of the research is promised.

The work done by Koethner and Aeuer upon the atomic weight of iodine is rather complex, and not easy to summarise (*Liebig's Ann. Chem.*, cccxxxvii., 124; Supple-

mentary Paper, p. 362; Preliminary Notice, *Ber.*, xxxvii., 2536). They first attempted to measure the ratio AgI : AgCl, and were surprised at obtaining values even lower than those found by Stas. This result was finally explained by the discovery that silver iodide, precipitated from a nitrate solution, carried with it inclusions of silver nitrate, which, however, together with silver chloride, was removable by long digestion with ammonia. The silver chloride produced from the iodide was found to volatilise to a small extent, and it was necessary to collect and estimate these traces. Finally, with iodide of silver from several sources, the following determinations were made, the weights being reduced to a vacuum. The calculations (for H = 1) were based upon Ag = 107.12 (107.93) and Cl = 35.18 (35.45).

Weight AgI.	Weight AgCl.	Atomic weight I.
24.88066	15.18917	125.982
10.24699	6.25565	125.980
12.57020	7.67391	125.981
9.62006	5.87286	125.982
12.26770	7.48902	125.988
22.60660	13.80058	125.988
20.98601	12.81162	125.981
22.47667	13.72122	125.988

Mean . . . 125.984

For O = 16 . . 126.936

In their supplementary paper, which was called forth by Baxter's research, the authors apply the new Richards and Wells value for chlorine to this mean value, which then becomes I = 126.964, in closer agreement with Baxter's determinations.

Koethner and Aeuer also made two syntheses of silver iodide by different methods. First, hydriodic acid was prepared from ethyl iodide, and used as the source of iodine. 34.51789 grms. Ag gave 75.12752 AgI. Hence, I = 126.026 for H = 1, or 126.978 when O = 16. In the second experiment iodine was purified by Stas' method, and the silver was burned in a stream of iodine vapour. 11.37544 grms. Ag gave 24.75691 AgI; hence, I = 126.011 for H = 1, or 126.963 when O = 16. The last value they regard as the most probable. In their latest paper they also give one more measurement of the ratio AgI : AgCl. 25.18868 grms. AgI gave 15.37678 AgCl. Hence, I = 126.008 (H = 1), or 126.968 (O = 16).

Finally, Koethner and Aeuer re-calculate their determinations of the AgI : AgCl ratios, and also Ladenburg's, with the data used by Baxter for his vacuum corrections.

	H = 1.	O = 16.
Koethner and Aeuer . .	126.004	126.964
Baxter	126.015	126.975
Ladenburg	126.028	126.988

From the mean of all the forty-one determinations made by Ladenburg, Scott, Baxter, and themselves they find I = 126.010 (H = 1) and 126.970 (O = 16).

Rubidium.

The determinations by Archibald (*Journ. Chem. Soc.*, lxxxv., 776) of the atomic weight of rubidium follow the lines of the investigation upon caesium which was published a year ago by Richards and Archibald. The chloride and bromide were the compounds analysed. From the chloride the following data were obtained, with all weights reduced to a vacuum and O = 16.

Archibald divides the foregoing determinations into four series, representing different samples of material, a procedure which need not be followed in an abstract like this. From all of the experiments the ratio between silver and silver chloride becomes 100 : 75.274. Stas found 75.276.

Weights.			Atomic weight Rb.	
RbCl.	AgCl.	Ag.	RbCl : AgCl.	RbCl : Ag.
1.99966	2.37070	1.78454	85.489	85.485
2.06480	2.44778	1.84241	85.496	85.503
2.29368	2.71960	2.04710	85.475	85.478
1.09495	1.29796	0.97702	85.502	85.503
2.14381	2.54118	1.91316	85.507	85.488
2.89700	2.43475	2.58550	85.482	85.479
2.19692	2.60452	1.96076	85.491	85.475
2.14543	2.54386	1.91462	85.473	85.486
2.12164	2.51557	1.89346	85.477	85.483
2.25777	2.67685	2.01515	85.482	85.471
2.18057	2.58528	1.94594	85.484	85.489
2.32699	2.75878	2.07668	85.488	85.484
4.00035	4.74233	3.56998	85.495	85.486
2.43440	2.88613	2.17233	85.488	85.496
Mean . . .			85.488	85.486

The bromide analyses were as follows:—

Weights.			Atomic weight Rb.	
RbBr.	AgBr.	Ag.	RbBr : AgBr.	RbBr : Ag.
2.68170	3.04578	1.74930	85.471	85.502
2.07280	2.35401	1.35230	85.486	85.479
2.10086	2.38589	1.37061	85.485	85.478
2.61044	2.96462	1.70300	85.484	85.486
3.84082	4.36215	2.50590	85.475	85.471
3.77852	4.29084	2.46502	85.499	85.488
4.34299	4.93210	2.83340	85.488	85.477
Mean . . .			85.484	85.483

The final mean adopted by Archibald for all of the determinations is Rb = 85.485. From the weights of silver and silver bromide the percentage of metal in the latter substance is 57.445—a value identical with that found by Stas.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxi., No. 15, April 10, 1905.

Heat of Formation of Sodium Hydride. Acidity of the Hydrogen Molecule.—M. de Forcrand.—The author performs a series of experiments to find the heat of formation of sodium hydride, using M. Moissan's method with a few modifications. The mean of four experiments is +25.80 cal. In spite of the difficulties, the author believes the possible error to be not more than 1 cal. By calculation, he finds that H₂ gas + Na sol. = NaH sol. + H gas . . . +16.6 cal., or H₂ sol. + Na sol. = NaH sol. + H gas . . . +16.00 cal. This figure gives the value of the acidity of the molecule of solid hydrogen. It is thus evident that the reaction NaH sol. + Na sol. = Na₂ sol. + H gas should absorb 16.60 cal. So the acidity of the second atom of hydrogen becomes -16.60 cal. instead of +18.88 cal. The difference is -35.48 cal.; this number expressing the negative influence of the atom of sodium.

Etherification of Glycerin.—Marcel P. S. Guédras.—Whilst preparing certain plastic materials from casein, glycerin, and acetic acid the author proves the formation of glyceric ethers. The reaction takes place very rapidly and there is a catalytic effect due to the casein or the glycerin; the formation of monoacetine according to

the equation $C_8H_8O_6 + C_4H_4O_4 - H_2O = C_{10}H_{10}O_8$ being proved. This formation leads to the conclusion that it is the casein which, whilst undergoing no chemical modification, plays an important part as a catalytic agent.

Liquefaction of Allene and Allylene.—MM. Lespiau and Chavanne.—The authors investigate the conditions of liquefaction of the two carbides C_3H_4 —allylene, $CH \equiv C - CH_3$; and allene, $CH_2 = C = CH_2$. Allene melts at $-146^\circ C.$, and boils at -32° under atmospheric pressure. The critical-point is $+120.75^\circ C.$ Allylene, $CH \equiv C - CH_3$, melts at $110^\circ C.$, and has boiling-point $-23.5^\circ C.$ and critical-point $+129.5^\circ C.$

Hydrogenation of Benzonitrile and Paratolunitrile.—A. Frebault.—The author effects the hydrogenation of benzonitrile and paratolunitrile by the use of nickel, and obtains the primary and secondary bases. The tertiary base has not been found at all in the products of the reaction.

Secondary Diazoamines.—Léo Vignon and A. Simonet.—The secondary diazoamines are prepared by the union of the diazo-derivatives of the primary amines with the fatty or aromatic secondary amines. The reaction is very easy with aniline, its substitution products, the toluidines, and the naphthylamines. Less satisfactory results are obtained with the xylinides, and no results with the aromatic amine acids. Amongst the substitution derivatives of aniline, sulphanilic acid gives rise to the azoic derivative, and not the secondary diazoamine derivative. These latter substances are not stable, except those which are derived from the secondary fatty amines. The secondary aromatic diazoamines are transformed by molecular transposition into azoics in the same way as the primary diazoamines and under the same conditions, i.e., in presence of an excess of the amine. Under the influence of dilute acids, the diazoic nitrogen is evolved, with formation of a phenol and the next secondary amine, $RN_2.NR'R'' + H_2O = R.OH + N_2 + NHR'R''$.

Acetol Hydrates.—André Kling.—The author proves the existence of acetol hydrates in the aqueous solutions of acetol by investigating the variations in the physical properties of these solutions, especially their viscosity. He uses MM. Varenne and Godefroy's method, slightly modified to increase the sensibility, and identifies the following hydrates: $-C_3H_6O_2.H_2O$, $C_3H_6O_2.2H_2O$, $C_3H_6O_2.4H_2O$, and $2C_3H_6O_2.11H_2O$.

Use of Ammonium Metals in Organic Chemistry. Preparation of Formenic Carbides.—Paul Lebeau.—The author makes a series of experiments on the action of sodammonium on the mono-substituted halogen compounds of the formenic carbides, methyl chloride, ethyl iodide, and propyl iodide.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxviii., No. 2, 1905.

Iodometric Determination of Sulphurous Acid in Alkaline Solution.—Otto Ruff and Willi Jeroch.—The authors, in investigating the titration of sulphurous acid in presence of sodium bicarbonate, find that direct titration with iodine solution does not give correct results, because in consequence of the catalytic action of the iodine ions, oxidation of the sulphite by the oxygen of the air occurs. If excess of iodine solution is added and the excess titrated with thiosulphate or arsenious acid, accurate results are obtained only if the above error is compensated by the oxidation of the thiosulphate solution to sulphuric acid instead of to tetrathionic acid by means of the hypiodous acid formed by the action of iodine on sodium bicarbonate. The amount of this oxidation depends upon the concentration of the hypiodous acid, and thus upon that of the bicarbonate and the carbonic acid. The first error causes too low results for the sulphurous acid and the second too high. The following inconvenient but not impossible method does away with both errors, viz.:—In the

first place the titration of the excess is avoided as far as possible, and, secondly, the action of the oxygen of the air is prevented by the addition of mannite to the solution to be titrated, and by working in an atmosphere of carbon dioxide.

Action of Halogens on Santonin.—E. Wedekind and A. Koch.—The product of the action of bromine on solutions of santonin in glacial acetic acid or chloroform has the empirical formula $C_{30}H_{37}O_6Br_3$. One bromine atom is combined as hydrobromic acid, and the compound is an oxonium complex double salt of hydrobromic acid, santonin, and santonin dibromide corresponding to the formula $C_{13}H_{16}O_2 \cdot \begin{matrix} CH_2 \\ CO < Br \end{matrix} \cdot C_{13}H_{16}O_2 \cdot \begin{matrix} CH_2 \\ CO < Br \end{matrix} \cdot A$

considerably better yield is obtained if the necessary quantity of hydrobromic acid is added to the mixture of bromine and santonin. The compound decomposes at 105° without previously fusing. It gives up bromine under the influence of light and heat and on addition of warm water; the bromine of the HBr is more firmly bound than the other two bromine atoms. The authors cannot by any method obtain a mono-brom santonin, the existence of which seems to be doubtful. If iodine and hydriodic acid are added to santonin the corresponding iodine compound is formed. It possesses similar properties to those of the bromide, but is more stable. Chlorine behaves quite differently, forming no addition compound of oxonium nature, but substitution products instead, di- and mono-chlor-santonin, $C_{15}H_{16}O_3Cl_2$ and $C_{15}H_{17}O_3Cl$.

Oxaluramide.—Martin Schenck.—Oxaluramide on being gently warmed with strong ammonia yields oxaminic acid, urea, and oxalic acid. The first two are formed according to the equation $C_3H_5N_3O_3 + H_2O = C_2H_3NO_3 + CON_2H_4$, while the formation of oxalic acid is probably due to a secondary reaction between the oxaminic acid formed and the strong ammonia. The author finds that oxaluramide is very stable towards boiling water, from which it crystallises out unchanged; on heating dry oxaluramide, water, ammonia, cyanic acid, cyanuric acid, and biuret are formed; it was observed that when ordinary cyanuric acid, which contained water of crystallisation or was moistened with water, sublimes, the sublimate gives the biuret reaction very distinctly; probably the following reaction occurs: $-C_3N_3O_3H_3 + H_2O = C_2N_3O_2H_5 + CO_2$.

Supposed Solubility of Auroso-auroic Oxide in Water.—L. Vanino.—In cold water auroso-auroic oxide gives a fine suspension of very small particles, but does not dissolve. This may readily be proved by simply shaking up with Kieselguhr or barium sulphate, and by making use of Pukall's clay filter. Barium sulphate or Kieselguhr easily bring down the suspended oxide which is retained by the clay filter. Muthmann's method of identifying a suspension by means of gum arabic also proves that the so-called solution is a colloid suspension similar to that obtained by treating a ferric salt with ammonia in the cold.

Gold Hydrosols.—L. Vanino.—Ordinary alcohol can be used for producing colloid hydrosols. Absolute alcohol does not act upon gold chloride, but if an alcoholic gold solution is poured into water a hydrosol is formed. Gold chloride must be present; auro-chloride of sodium only acts in very dilute solution, no reaction occurring in concentrated solution. Methyl alcohol also produces similar colloid hydrosols.

Fusel Oil.—Hans H. Pringsheim.—The author has isolated from American potatoes a bacillus which may be partly responsible for the potato fermentation observed by Emmerling. Sterilised potatoes, on addition of this bacillus, yield an oil which smells strongly of amyl alcohol, and distils over between 112° and 130° . Three forms of these bacteria were observed; one of these, which is very much smaller than ordinary potato bacillus when it acts on potatoes, gives rise to a distinct odour of amyl alcohol. It forms spores on the potato at 35° ; these are readily

recognised by the various colourations produced. The experiments do not clearly show how far this form is responsible for the formation of fusel oil during yeast fermentation, and it does not appear that they cause the formation of the higher alcohols in distilleries.

Colloid Selenium.—C. Paal and Carl Koch.—If an aqueous solution of selenious acid is introduced into a solution of the sodium salt of protalbinic or lysalbinic acid a precipitate forms, which is removed by the addition of soda-lye. On warming this mixture no reduction takes place, and hydrazine hydrate has no effect in alkaline solution. But if dilute hydrochloric acid is added reduction takes place, nitrogen being evolved. The liquid turns red, and on addition of more acid red flakes of the absorption compound of colloid selenium with free protalbinic or lysalbinic acid separate out. The precipitate is insoluble in water, but soluble in caustic and carbonic alkalis. As finely divided selenium is slowly dissolved in the cold by caustic alkali, forming alkali selenide, sodium carbonate was used as a solvent. The colloid solutions thus obtained were purified by dialysis. By cautious evaporation the hydrosols were obtained in the solid stable soluble form; these precipitates when dried retain their solubility in alkalis, and by this method preparations containing a high percentage of colloid selenium can be obtained. Hydroxylamine salts may be used as reduction agents instead of hydrazine hydrate.

Brown and Blue Modifications of Colloid Tellurium.—C. Paal and Carl Koch.—Tellurium dioxide when treated with hydrazine hydrate gives the brown modification of colloid tellurium, while telluric acid yields a blue-grey or steel-blue liquid hydrosol. Other reduction agents always give the brown modification. The authors have prepared the adsorption compounds of colloid tellurium in combination with the sodium salt of protalbinic and lysalbinic acids, using hydrazine hydrate and hydroxylamine as reducing agents. The reaction between telluric acid, sodium protalbinic or lysalbinic acid, and hydrazine hydrate takes place in alkaline solution on warming; it begins at 40° to 50°, and proceeds fairly rapidly on the water-bath. Only the brown modification forms, and its colour does not change on boiling for a long time, or on addition of neutral salts (NaCl). Finally, after boiling for hours it is partially converted into hydrogel. Tellurium dioxide is reduced with much more difficulty by hydrazine hydrate in neutral or alkaline solution. The reduction of telluric acid by hydroxylamine and tellurium dioxide by hydrazine hydrate in alkaline solution and in presence of a decomposition product of albumen, always gives rise to the brown modification of tellurium hydrosol. By continued boiling this is gradually changed into the blue modification. The "new modification of colloid tellurium," recently described by Gutbier and Resenschek, is undoubtedly a mixture of the two modifications. By cautious evaporation both modifications can be obtained in the solid form, which is soluble in water, and can be heated for some time to 100° without suffering any change. On addition of acids to their aqueous solutions the adsorption compounds of the two hydrosols forms with free protalbinic or lysalbinic acid separate out. The authors thus obtained stable products containing over 80 per cent tellurium; the blue modification is less stable than the brown, and is converted into the hydrogel after it has been kept for a year in the solid state. The preparations containing the brown modification can be kept for three years, provided that they are preserved from oxidation. In preparations of either modification, if exposed to the air, the hydrosol is gradually converted into tellurium dioxide.

Action of Hydrofluoric Acid on Nitrogen Tetrasulphide.—Otto Ruff and Curt Thiel.—On heating nitrogen tetrasulphide with hydrofluoric acid small quantities of a gas soluble in caustic potash are obtained. This gas is decomposed by water into hydrofluoric acid and sulphurous acid, ammonium fluoride being also formed. The gas is pure thionyl fluoride, first prepared by Moissan,

its oxygen being derived from traces of H₂O and also from traces of copper oxide present. The authors prepared the substance in a specially constructed iron cylinder with copper lined cover, and fitted with copper exit tubes. The N₄S₄ and anhydrous HF were heated to 100 for two hours; then the cylinder was cooled in liquid air and opened, the gas being driven by means of a current of hydrogen into a glass vessel cooled by liquid air. The residue consisted of copper sulphide, sulphur, copper fluoride, and ammonium fluoride. Only very small quantities could be prepared thus. It was found that the presence of some copper was essential to the formation of thionyl fluoride. The gas does not react with pure chlorine, bromine, or nitrogen. In presence of carbon or in sunlight chlorine decomposes it with the aid of the glass of the containing vessel, giving 2SOF₂ + 2Cl₂ + SiO₂ SiF₄ + 2SO₂Cl₂. With nitrous anhydride nitrosulphonic acid and silicon tetrafluoride are formed. The gas is very stable at high temperatures.

Action of Potassium Iodide on Bromanil and Chloranil.—Henry A. Torrey and W. H. Hunter.—If potassium iodide is heated with a solution of bromanil in acetone the liquid becomes green, and then turns red, some free iodine being formed. On removing the excess of undissolved reagents by filtration the cooled filtrate yields a crystalline product which may be purified by dissolving in acetic ether. It forms red-brown prisms or golden-brown plates, and has the formula C₆O₂Br₂I₂, being thus a dibrom-di-iodo benzo-quinone. This substance, like other quinones, forms addition products with amines; it may easily be reduced to a colourless body which is probably the corresponding hydroquinone. Chloranil partly dissolved in acetone is readily attacked by finely powdered potassium iodide in the cold, giving a substance which contains potassium, and is decomposed by water, yielding an insoluble compound and a purple solution. Bromanil forms a similar derivative under the same conditions.

Separation of Silver from Lead.—Hj. Lidholm.—The separation of silver from lead by the method which depends upon the different behaviour of their iodides towards dilute nitric acid is not satisfactory when small quantities of silver are present in much lead. It is found to be very tedious, and also requires considerable skill. The separation of small quantities of silver from much lead cannot be performed by removing the lead either by means of hydrogen peroxide or potassium bichromate in alkaline solution. The author has devised a method of separation depending upon the fact that many organic compounds, especially phenols, reduce silver from its solutions, while most phenols give very difficultly soluble phenolates with lead. Hydroquinone, however, does not precipitate lead. Silver is not separated quantitatively if the solution contains free mineral acids, but all the silver will be precipitated if sodium acetate is added to the nearly neutral solution, so that the only free acid present is acetic acid. The alloy or mineral is dissolved in the usual way with addition of tartaric acid, the solution filtered and neutralised, and sodium acetate added. Any precipitate of basic lead acetate thus formed is dissolved in acetic acid, and the solution heated to boiling. Then some c.c. of hydroquinone solution are added (2 c.c. of a 4 per cent hydroquinone solution are sufficient to reduce 0.1 gm. Ag), when the silver separates out instantly. It is then allowed to stand, and filtered, the precipitate being washed with water containing some ammonium nitrate to facilitate filtration. The silver is then dried, ignited in a porcelain crucible, and weighed. Of other metals of the same group, cadmium does not affect this method of separation; copper is partly reduced and partly precipitated as phenolate, and bismuth is partly reduced. Hence, if these metals are present, after the method has been carried out exactly as above, any bismuth compounds separated out are removed by filtration. The filtrate is precipitated with hydroquinone, the precipitate brought on to the filter, and dried and ignited, and then introduced into a beaker. The residue is dissolved in nitric acid, and the nitrates formed

are washed into the beaker. Some c.c. of concentrated nitric acid are now added to dissolve the whole, and the silver is precipitated with hydrochloric acid. The precipitate, which contains silver chloride as well as basic bismuth chloride, is separated off; it may then be treated by Fresenius's method. The other metals of the group can be determined in the usual way after the silver has been separated. The method is accurate, even if only 0.01 per cent of silver is present in the lead.

New Method of Determining Mo_2O_3 and V_2O_5 in presence of one another.—B. Glasmann.—If a mixture of molybdic and vanadic acids is treated with zinc vanadium dioxide and molybdenum sesquioxide are formed, while with magnesium vanadium trioxide and molybdenum sesquioxide result. If these are treated with permanganate the following reactions occur:—
(a) $5\text{V}_2\text{O}_5 + 5\text{Mo}_2\text{O}_3 + 15\text{O}_2 (12\text{KMnO}_4) = 5\text{V}_2\text{O}_5 + 10\text{MoO}_3$,
(b) $5\text{V}_2\text{O}_5 + 5\text{Mo}_2\text{O}_3 + 25\text{O}_2 (10\text{KMnO}_4) = 5\text{V}_2\text{O}_5 + 10\text{MoO}_3$.
Thus, from equation (a) $6\text{KMnO}_4 = 5\text{V}_2\text{O}_5$ and $6\text{KMnO}_4 = 10\text{MoO}_3$ and from (b) $4\text{KMnO}_4 = 5\text{V}_2\text{O}_5$ and $6\text{KMnO}_4 = 10\text{MoO}_3$. To determine the amount of the constituents present in a mixture of M_2O_3 and V_2O_5 two given volumes of the solution were heated for from one to one and a-half hours, the one with zinc and hydrochloric acid, and the other with magnesium and hydrochloric acid. The solutions thus obtained were introduced into a porcelain dish containing 10 grms. of manganous sulphate in 300 c.c. of boiling water, and titrated with permanganate ($\frac{1}{2}$, -1). The difference in the two quantities of permanganate used represents that required for the oxidation of V_2O_5 to V_2O_6 , and three times this difference represents the permanganate required to oxidise V_2O_5 to V_2O_6 . Hence, the per cent of the latter can be calculated ($6\text{KMnO}_4 = 5\text{V}_2\text{O}_5$). The excess of permanganate used for the first titration represents the quantity necessary to oxidise Mo_2O_3 to 2MoO_3 , from which the MoO_3 can be calculated ($6\text{KMnO}_4 = 10\text{MoO}_3$). Calculations on the basis of equation (b) would of course lead to the same results.

Absorption of Oxygen by Alkali Vanadates.—Wilhelm Prandtl.—If vanadium pentoxide is fused with about 10 per cent of alkali carbonate or phosphate, crystals of the vanadico-vanadate of the alkali are formed. These compounds fuse in air at a dark red heat, taking up as much oxygen as is necessary to convert all the vanadium into pentoxide, and thus pass into acid vanadates. On lowering the temperature they crystallise out in the original form, at the same time giving up the oxygen they have absorbed. Thus this is a case of the dissociation of a compound rich in oxygen into free oxygen, and a compound containing less oxygen as the temperature falls. In preparing sodium vanadico-vanadate ($5\text{V}_2\text{O}_5 \cdot \text{V}_2\text{O}_4 \cdot \text{Na}_2\text{O}$) all the phenomena-recalling a miniature volcano, as observed by Dumas, were seen. The compound forms steel-blue (probably) rhombic crystals, insoluble in water and unaffected by concentrated nitric acid, even on boiling. They are slowly oxidised by hot dilute ammonia, and dissolve in concentrated sulphuric acid. The potassium compound has similar properties, but the decomposition is $8\text{V}_2\text{O}_5 \cdot \text{V}_2\text{O}_4 \cdot \text{K}_2\text{O}$. Both compounds absorb oxygen on fusing in air, forming acid vanadates; when the temperature is lowered they give up this oxygen and again assume their original composition. If they are fused in air and then while still molten brought into an atmosphere of CO_2 they give up their oxygen on solidifying, but in an atmosphere containing no oxygen they either do not fuse at all or else only at a much higher temperature. All the oxygen absorbed is not given up, but the quantity absorbed corresponds approximately to that necessary for the oxidation of vanadico-vanadate to acid vanadate.

Institute of Chemistry.—The Intermediate and Final (A.I.C.) Examinations will be held in the Laboratories of the Institute on Tuesday, the 4th of July next, and not as in previous advertisements in our columns, the 24th of July.

MEETINGS FOR THE WEEK.

- MONDAY, 15th.—Society of Arts, 8. (Cantor Lecture). "Use of Electricity in Mines," by H. W. Ravenshaw, Assoc. M. Inst. C.E.
- TUESDAY, 16th.—Royal Institution, 5. "The Study of Extinct Animals," by Prof. L. C. Miall, F.R.S., &c.
- Society of Arts, 8. "Excavation of the Oldest Temple at Thebes," by H. R. Hall, M.A.
- WEDNESDAY, 17th.—Microscopical, 8. "The Movements of Diatoms and other Microscopic Plants," by D. D. Jackson. Exhibition of Slides of the Oribatidae.
- Society of Arts, 8. "The Use of Wood-pulp for Paper-making," by S. C. Phillips.
- Chemical, 5.30. "Chlorination of Methyl Derivatives of Pyridine—Part I. 2-Methyl Pyridine," by W. J. Sell. "Absorption Spectra of Uric Acid, Murexide, and the Ureides in relation to Colour and to their Chemical Structure," by W. N. Hartley. "Further Studies on Dihydroxymaleic Acid," by H. J. H. Fenton. "Thermal Decomposition of Formaldehyde and Acetaldehyde," by W. A. Bone and H. L. Smith. "Synthesis of Formaldehyde," by D. L. Chapman and A. Holt, jun. "Influence of Light on Diazo Reactions," by K. J. P. Orton, J. E. Coates, and (in part) F. Burdett.
- THURSDAY, 18th.—Royal Institution, 5. "Flame," by Prof. Sir James Dewar, F.R.S., &c.
- Society of Arts, 4.30. "Plague in India," by Charles Creighton, M.D.
- Faraday Society, 8. "Application to Electrolytes of the Hydrate Theory of Solutions," by T. M. Lowry, D.Sc.
- FRIDAY, 19th.—Royal Institution, 9. "The Native Races of the British East Africa Protectorate," by Sir Charles Eliot, K.C.M.G.
- SATURDAY, 20th.—Royal Institution, 3. "Evolution of the Kingship in Early Society," by James G. Frazer, D.C.L., LL.D., Litt.D.

COUNTY OF ESSEX.

APPOINTMENT OF PUBLIC ANALYST.

THE COUNTY COUNCIL OF ESSEX are prepared to receive Applications for the Post of PUBLIC ANALYST. Applications, accompanied by not more than three recent testimonials, must be sent to my Office, not later than the 24th day of MAY, enclosed in an envelope marked "Public Analyst."

The appointment will date from JULY 1st, 1905, and will be subject to the approval of the Local Government Board, and will be held during the pleasure of the Council, subject to three months' notice on either side.

The person appointed must be duly qualified, and will be required to perform all the duties of a Public Analyst in accordance with the provisions of the Statutes relating to the sale of Food and Drugs. He will be required to furnish such proof of competency as the County Council and the Local Government Board may require.

The salary offered is a retaining fee of £200 per annum and 5s. for each sample analysed (whether submitted by authorities or others), which is to cover the Analyst's trouble, loss of time, travelling, and other expenses. About 1400 samples were analysed during 1904.

The selected Candidate will be required to give security for the due performance of his office by a Bond in the London Guarantee and Accident Company, Ltd., for £100.

Candidates must comply with the Standing Orders of the County Council relating to the appointment of Officers, a copy of which will be forwarded on application.

Shire Hall, Chelmsford,
May 9th, 1905.

HERBERT L. GIBSON,

Clerk of the Council.

INSTRUCTION IN

PURE CULTIVATION OF YEAST.

Courses for Beginners, as well as for Advanced Students, in Physiology and Technology of Fermentations. Biological Analysis of Yeast. The Laboratory possesses a numerous collection of Yeasts (Brewers', Distillers', Wine, Disease Yeasts), Moulds, and Bacteria. *Manuals:* Alfred Jörgensen, "Micro-organisms and Fermentation" (London and New York, Macmillan & Co., 1900); and "The Practical Management of Pure Yeast" (London, "The Brewing Trade Review," 1903).

The Laboratory supplies for direct use Pure Cultures of Yeast for Breweries, Distilleries, Wine Manufactories, &c., and performs Analyses of Yeasts, &c.

Further particulars on application to the Director—

ALFRED JÖRGENSEN, The Laboratory,
Copenhagen V., Denmark.

THE CHEMICAL NEWS.

VOL. XCI., No. 2373.

THE ELUCIDATION OF THE THORIUM PROBLEM.

By CHARLES BASKERVILLE.

HERR R. J. MEYER has undertaken to repeat my experiments relating to the elementary character of thorium, and to submit them to a critical examination; he has published the results obtained by him in the *Berichte*, 1905, xxxviii., 817. I consider it most desirable that there should be many collaborators in the field of the research which I have chosen, for the truth can be discovered only by many careful repetitions of the experiments I have performed, and also by the strict criticism both of the methods used and also of the results to which they lead. I must, however, make one request, and that is that the conditions under which I worked may be maintained as exactly as possible. Thus, for example, it does not appear to me to be a matter of indifference whether I heat a substance in a current of chlorine with carbon, or in chlorine and a current of sulphur chloride; also the maintenance of definite temperatures is of fundamental importance. I do not bring this forward with the intention of criticising Herr Meyer's work, but only so save any loss of time. I shall shortly publish an account of the exact conditions under which my experiments were performed in order to enable all those who are interested in this most important question to decide whether they can confirm my results or not.—*Berichte*, xxxviii., No. 6, 1444.

THE INFLUENCE OF RADIUM RAYS UPON CHLORINE DETONATING GAS.

(FIRST COMMUNICATION).

By W. P. JORISSEN and W. E. RINGER.

THE importance of the new radiations from a chemical point of view has been but little investigated; the number of reactions known which are accelerated or produced by the influence of Becquerel rays, for example, is not large. The chemical effect of these rays which was first observed was, of course, that upon the photographic plate, described by Becquerel.

P. Curie and Mme. S. Curie (*Comptes Rendus*, 1899, cxxix., 823; see also Giesel, *Verhandl. d. Deutsch. Phys. Ges.*, Jan. 5, 1900) observed that they convert oxygen into ozone, Becquerel (*Comptes Rendus*, 1901, cxxix., 709) that they have the same effect as light upon a solution of mercuric chloride and oxalic acid, i.e., he found that a little calomel is gradually formed. Also ordinary phosphorus is changed into the red modification. The Curies observed the colouration of glass and porcelain, Giesel (*Verhandl. d. Deutsch. Phys. Ges.*, Jan. 5, 1900; *Berichte*, 1902, xxxv., 3609) that of fluorspar, alkali haloids, and paper by radium rays. Hardy and Miss Wilcoke (*Proc. Roy. Soc.*, 1903, lxxii., 200; van Aubel, *Phys. Zeit.*, 1904, v., 637) studied the effect of these rays upon solutions of iodoform in various solvents, especially in chloroform in presence of oxygen. Hardy further observed an effect upon the coagulation of globulin (*Proc. Physiol. Soc.*, May 16, 1903). (For the physiological effects of radium rays cf., among others, Mme. Curie, "Untersuch. über d. Radioact. Substanzen," translated by Kaufmann, Braunschweig, 1904, 90-92; Rutherford, "Radio-activity," 1904, 176-177).

Fenton (*Proc. Camb. Phil. Soc.*, xii., 260) found that the decomposition of hydrogen peroxide was accelerated by radium rays, and Skinner (*Ibid.*, xii., 424) observed a brown colouration of mercurous sulphate.

The decomposition of water by radium is known from the experiments of Runge and Bodländer (Giesel, *Berichte*, 1902, xxxv., 3605), as well as those of Ramsay and Soddy (*Proc. Roy. Soc.*, 1903, lxxii., 204).

Other chemical effects of radium rays were observed by Pellini and Vaccari (*Atti. Accad. dei Lincei*, Sept. 4, 1904, [5], xlii., 269). They noticed an effect upon aqueous hydriodic acid, and on solutions of propyl and isopropyl iodide in chloroform, but they observed no effect upon chlorine detonating gas. In these last experiments they used the arrangement of Bunsen and Roscoe, with some modifications. The insulation vessel was shaped like Dewar's vacuum vessel; the little tube with radium bromide could be introduced into the opening; it contained 5 m.grms. (from the chemical manufactory of Dr. Rich. Shamer, Hamburg).

In some of the experiments it was covered with thin aluminium foil, in order to intercept the phosphorescence light, and then with a second little tube; in other experiments the aluminium foil and the second tube were omitted.

De Hemptinne* has performed some experiments on the effect of Röntgen rays on chlorine detonating gas. The gas was contained in a glass vessel with an aluminium cover, which was protected from the action of the chlorine by means of paraffin. He allowed the Röntgen rays to penetrate into the gaseous mixture through this aluminium plate, but could detect no effect, even after an hour.

After investigating the chemical effects of radium rays for several months, we turned our attention to chlorine detonating gas. From De Hemptinne's experiments with Röntgen rays it was at least probable that the effect could only be feeble.† Moreover, we had then only 5 m.grms. of radium bromide at our disposal (pure, from the chemical manufactory of Dr. Rich. Shamer, Hamburg).

After it had appeared from preliminary experiments that the effect, if any, was at all events exceedingly feeble, we endeavoured to make the apparatus and gaseous mixture as sensitive as possible.

In the main we also used Bunsen and Roscoe's arrangement (Ostwald's "Klassiker," Nos. 34 and 38). The chlorine detonating gas was prepared electrolytically from 25 per cent pure hydrochloric acid in the vessel A, using electrodes of graphite (from the firm of Warmbrunn, Quilitz, and Co., Berlin, N.), which were inserted into a rubber cork covered with paraffin. Four Bunsen elements were employed.

The chlorine detonating gas was washed with water in D and E; the washing flask E was connected with the three-way cock G by means of the bulb F. By means of this cock the gaseous mixture was at first led into alkali, when it had to overcome as nearly as possible the same pressure as later, when it was led through the apparatus. This last operation was continued for some days.

A small tube, J, was melted into the "insulation vessel" H. The lower half of this tube consisted of very thin glass. The radium bromide tube, also made of very thin glass, was introduced, by means of a thread attached with sealing-wax, into the tube of the vessel H, into which it exactly fitted. In this was about 2 c.c. of water. The washing flask L was so arranged that, on passing the chlorine detonating gas through it, it had to overcome about the same pressure as was afterwards exerted by the water from the washing flask L upon the gaseous mixture in the horizontal tube K. By a short illumination, it could easily be brought to the extreme end of the horizontal

* *Zeit. f. physikal. Chem.*, 1896, xxi., 495. However, these experiments, on being exceedingly carefully repeated, might lead to a different result.

† Pellini and Vaccari's research first came to our notice at the end of October, through the report of it in the *Chem. Centralblatt*, 1904, ii., 1197).

‡ The figure represents about one-fifth the actual size.

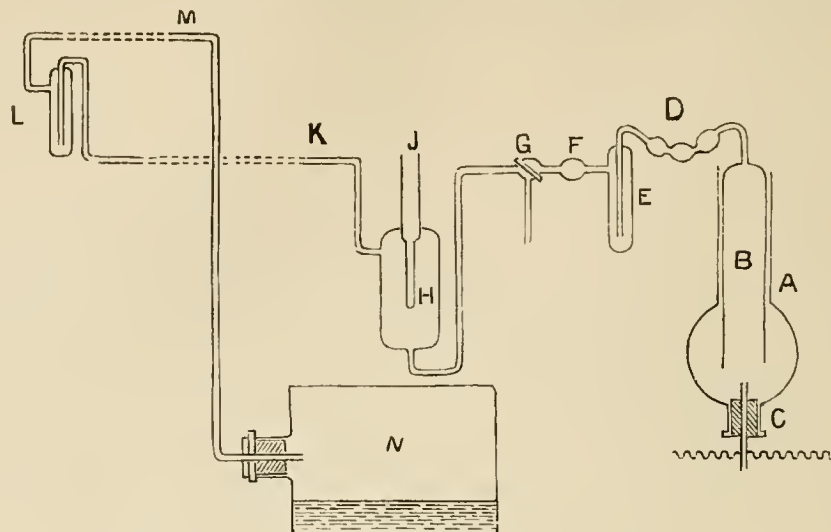


TABLE I.—Radium Tube Uncovered.

Time, in hours.	Position of meniscus, in m.m.	Time, in hours.	Position of meniscus, in m.m.
0	110	71	176
1'5	109	95'5	215 (b)
3'5	110	101'5	215
5'5	109	120'5	218'5
23	112 (a)	144'5	220'5 (a)
25'5	111'5	146'5	222
27'5	127	150'5	246
30	129	167	308
47	141	170	312 (b)
53'5	150	172	312'5

TABLE II.—Radium Tube Black.

Time, in hours.	Position of meniscus, in m.m.	Temperature.
0	490	25'20
20	487'5	25'50
26'50	490	25'40
45'50	495	25'30
49'50	504	25'30
50'50	497'5	25'25
68	508 (a) (c)	25'20
74'50	503	25'27
92	559	25'20
95'25	559 (b)	25'23
96'25	558 (d)	25'35
98'75	548	25'23
120'25	535 (a)	25'24
139'75	600	25'23
141'75	608 (b)	25'30
146'75	611	25'27
164'25	612'5	25'25
170'25	601 (a)	25'26
178'25	600	25'20
188'25	637	25'30
190'75	657 (b)	25'30
193'25	654	25'25

(a) Radium tube introduced.

(b) Radium tube taken away.

(c) On representing these numbers graphically, it is seen that the curves which the observations during the presence of the radium bromide give are parallel; hence the rate was the same in the three cases.

(d) Thermostat replenished.

tubes. This arrangement allowed a state of equilibrium to be reached fairly soon after the gases had been led through the apparatus.

The horizontal tube K was about 75 c.m. long and had a diameter of 2 m.m.; it was provided with a scale made of paper and graduated in m.m. The "insulation vessel" H was placed in a thermostat which, by means of a toluene regulator, was kept at 25°; it was stirred by an aluminium stirrer driven by a small gas flame covered with zinc to prevent illumination.

When the gaseous mixture had been led through the apparatus, the washing flask L was connected with the litre flask N by means of a little piece of thick-walled rubber tubing, which was then immersed under mercury, and a thin glass tube. The flask N was placed at the bottom of the thermostat, and in it was enough mercury covered with a layer of water to keep it under water.

This arrangement was found necessary in order to be independent of barometrical fluctuations and the consequent disturbances in the apparatus.

It appeared that the stirring arrangement was not energetic enough for the purpose, and a more rapid turning with the hand always caused a slight movement of the water meniscus in the tube K.

The whole apparatus was placed in the dark room. Moreover, the vessel H was surrounded with a zinc box; the tubes were either varnished black or covered with black paper.

In the first experiments the radium bromide tube was not covered in the "insulation vessel"; afterwards it was covered with black varnish to stop the phosphorescence light.

In some experiments equilibrium was established only very slowly, without any cause being apparent, and in others the chlorine detonating gas was very little sensitive to light.

The sensitiveness was tested by means of a candle flame at a distance of about one-half metre from the window of the thermostat; the zinc covering of the vessel was then of course removed.

It is our intention to repeat these experiments with dry chlorine detonating gas and with a larger quantity of radium bromide, and to examine the influence of the radium rays on the period of induction, illuminating with a constant flame (Bunsen and Roscoe, *loc. cit.*; Pringsheim, *Wied. Ann.*, 1887, xxxii., 384). It would perhaps be interesting to study a possible influence on the phenomenon of the sudden expansion of chlorine detonating gas on momentary illumination.—*Berichte*, 1905, xxxviii., 899.

DETERMINATION OF VAPOUR-PRESSURE
BY AIR-BUBBLING.*

By EDGAR PHILIP PERMAN and JOHN HUGHES DAVIES.

It was shown recently by one of us that the vapour-pressure of water can be determined with a considerable degree of accuracy by bubbling a current of air through water in a thermostat, and estimating the amount of water evaporated by absorbing it in strong sulphuric acid (*Proc. Roy. Soc.*, 1903, vol. lxxii., p. 72).

The accuracy of the method has since been questioned, supersaturation being specially suggested as likely to cause error (*Journ. Phys. Chem.*, 1904, vol. viii., pp. 299 and 313). We have therefore made experiments in order to discover what error (if any) is introduced by supersaturating the air with moisture before it enters the water in the thermostat. The effect of dust in the air and of electrification have also been investigated. In each case the arrangement of the apparatus was as described in the previous paper.

Supersaturation.—Before passing into the flasks in the thermostat, which was maintained at 70°, the air was bubbled through a large wash-bottle containing water at about 85°. The wash-bottle was connected by a short rubber tube with the flasks at 70°. Otherwise the experiment was conducted as already described. The following results were obtained:—

W.	P.	T.	V.	p.	Vapour-pressure.
Grm.	M.m.	°C.	Litres.	M.m.	M.m.
0.6757	753.2	286.1	2.005	736.4	234.7
0.6706	749.3	288.1	2.005	730.2	234.8

The numbers obtained in the previous experiments were 234.2, 233.2, 234.5, 235.0, 233.5, and 233.5, while Regnault's number (corrected as described in the former paper) is 234.0. The supersaturation of the air with moisture caused, therefore, no appreciable effect, the air assuming the normal state of saturation on passing through the four flasks in the thermostat. An explanation of the erratic results obtained by Carveth and Fowler (*Journ. Phys. Chem.*, 1904, viii., 299, 313) has already been offered by one of us (*Journ. Phys. Chem.*, 1905, ix., 36).

Dust in the Air.—A thick smoke was made by burning pieces of phosphorus near the inlet tube of the apparatus described in the former paper. The smoke was maintained during the whole of the experiment. The result was as follows:—

W.	P.	T.	V.	p.	Vapour-pressure.
Grm.	M.m.	°C.	Litres.	M.m.	M.m.
0.3347	751.8	288.9	1.003	732	235.2

Although a little high, the result can hardly be taken to indicate that the fumes of phosphorus pentoxide had any effect on the amount of water carried off. No doubt there was such an effect in the first flask, but the state of the air became normal before it left the last one. The experiment was not repeated owing to its disagreeable character.

Electrification of the Air.—1. The air was made to pass through a large flask in which hydrogen was being rapidly evolved from zinc and dilute sulphuric acid; the air was thus mixed with electrified hydrogen; it was filtered from the acid spray by a plug of cotton-wool. The result was—

W.	P.	T.	V.	p.	Vapour-pressure.
Grm.	M.m.	°C.	Litres.	M.m.	M.m.
0.3395	763.4	283.4	1.002	747.5	234.7

The effect of the electrification was probably limited to the first or first and second flasks, the result obtained again being normal.

2. One terminal of an induction-coil, capable of giving (with the battery power used) a 6-inch spark, was connected with a wire passing into the first (nearest the inlet) flask in the thermostat; the other terminal was connected with the bath, so that the silent discharge passed through the flasks and the air inside. The result was normal.

W.	P.	T.	V.	p.	Vapour-pressure.
Grm.	M.m.	°C.	Litres.	M.m.	M.m.
0.3365	763.4	283.8	1.002	747.3	233.6

3. The X-rays from an ordinary focus-tube were allowed to fall on the flasks in the thermostat, and were specially directed on to the last (nearest outlet). A wire from one of the terminals of a Wimshurst machine was passed down the gauge-tube into the last flask, the other terminal being connected with the bath. With this double arrangement it was thought that the air in the last flask must be strongly electrified and produce a fog. It was impossible to see whether there was a fog or not, but the effect on the vapour-pressure was as expected.

W.	P.	T.	V.	p.	Vapour-pressure.
Grm.	M.m.	°C.	Litres.	M.m.	M.m.
0.3473	761.9	282.3	1.002	746.7	237.5
0.3473	761.4	282.9	1.002	745.8	238.0

The greatest deviation from the normal value obtained in these experiments—with the exception of the last two—is slightly over 0.5 per cent, which is almost exactly the same as that obtained in the original investigation.

It may safely be concluded, therefore, that no naturally occurring supersaturation, or dust, or electrification of the air would have any appreciable effect on the result.

TWELFTH ANNUAL REPORT
OF THE COMMITTEE ON ATOMIC WEIGHTS.
DETERMINATIONS PUBLISHED IN 1904.*

By F. W. CLARKE.

(Continued from p. 221).

Glucinum.

THE re-determination by Parsons (*Journ. Am. Chem. Soc.*, xxvi., 721) of the atomic weight of glucinum is notable both for its thoroughness and for its novelty. After a careful investigation of the halide salts of glucinum and of the sulphate, which were found to be unsuitable for exact work, two new methods of determination were adopted. In one series the acetylacetonate, $\text{Gl}(\text{C}_5\text{H}_7\text{O}_2)_2$, purified by repeated sublimations, was reduced by ignition to oxide. In the other series the volatile basic acetate, $\text{Gl}_2\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$, was similarly treated. All weights were reduced to a vacuum, and the oxide obtained was also examined and corrected for occluded gases. The final figures for the two series are given below, with reduction based upon O = 16.

Weight acetylacetonate.	Weight oxide.	Atomic weight Gl.
2.62245	0.31798	9.142
3.28037	0.39757	9.129
2.08993	0.25286	9.081
2.41401	0.29233	9.105
1.61353	0.19554	9.127
1.39714	0.16905	9.083
1.85023	0.22419	9.122

Mean 9.113

Weight basic acetate.	Weight oxide.	Atomic weight Gl.
1.89291	0.46788	9.139
1.47931	0.36534	9.111
1.09012	0.26911	9.097
1.35642	0.33493	9.105
1.56787	0.38715	9.106
1.34465	0.33204	9.106
2.61484	0.64630	9.137
2.67721	0.66109	9.107
3.11534	0.76930	9.107

Mean 9.113

Tanatar (*Journ. Chem. Soc.*, lxxxvi., ii., Abst., 335, from *Journ. Russ. Chem. Soc.*, xxxvi., 82) has endeavoured to

* From the *Journal of the American Chemical Society* xxvii., No. 3.

* A Paper read before the Royal Society, March 30, 1905.

show that glucinum is a tetrad element, with an atomic weight double that which it is commonly assigned. The specific heat of the metal at low temperatures accords best with this view. The suggestion, however, does not seem to be entitled to much weight. Very recently Pollok (*Journ. Chem. Soc.*, lxxxv., 1630) has brought forward evidence indicating that ordinary glucinum contains an admixture of an oxide of higher molecular weight. Fractional distillation of the chloride gave portions much more volatile and of higher molecular weight than the ordinary compound, and spectroscopic differences were also noted. If this research should be confirmed, the atomic weight of the true glucinum would be lowered.

Aluminium.

The work of Kohn-Abrest (*Comptes Rendus*, cxxxix., 669), at least so far as it has been published, adds little or nothing to our knowledge of the atomic weight of aluminium. A metal containing 98.68 per cent of aluminium, with known impurities, was dissolved in hydrochloric acid, and the hydrogen evolved was burned over copper oxide. From the weight of water formed the atomic weight was calculated, with $O = 15.88$. The mean of seven experiments gave $Al = 27.05$. In a single experiment 0.3429 grm. Al gave 0.6444 grm. Al_2O_3 . Hence $Al = 27.09$. Until more details of the work have been published, the value of these experiments must remain problematical.

Indium.

In Thiel's research upon the atomic weight of indium (*Zeit. Anorg. Chem.*, xl., 280; Preliminary Notice, *Ibid.*, xxxix., 119, and *Ber.*, xxxvii., 175), several methods of determination were investigated. The conversion of the metal, through its nitrate, into the oxide gave values ranging from 113.42 to 115.6, a variation due to unavoidable errors in the process. On the one hand, indium oxide is somewhat volatile, and on the other, it tends to occlude impurities, which are probably for the most part, gaseous. It is also hygroscopic. Indium oxide, therefore, is at present an unsatisfactory compound to employ for measurements of this kind.

With indium trichloride better results were obtained. The following data represent vacuum weights, with all corrections applied. The calculations are based on $O = 16$.

Weight $InCl_3$.	Weight $AgCl$.	Atomic weight In .
5.0194	9.7526	115.03
4.7049	9.1401	115.07
5.7067	11.0862	115.07
5.4075	10.5055	115.06

Mean . . . 115.05

Incidentally, and as a check upon these determinations, two analyses were performed with potassium chloride.

Weight KCl .	Weight $AgCl$.	Atomic weight K .
7.4314	14.2903	39.11
7.4321	14.2939	39.10

With the tribromide a somewhat lower value for indium was found. The final, but uncorrected, data are subjoined.

Weight $InBr_3$.	Weight $AgBr$.	Atomic weight In .
8.9040	14.1531	114.74
8.2140	13.0512	114.88
9.4016	14.9422	114.79

Mean . . . 114.80

The cause of the difference is unexplained, and further investigation is promised. Meanwhile, the value $In = 115$ is the most probable.

It should also be mentioned that Dennis and Geer have undertaken to determine the atomic weight of indium, and a preliminary notice by them on the purification of the metal has already appeared (*Journ. Am. Chem. Soc.*, xxvi., 437, and *Ber.*, xxxvii., 961).

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, May 4th, 1905.

Professor R. MELDOLA, F.R.S., President, in the Chair.

MR. J. W. WILKINSON was formally admitted a Fellow of the Society.

A certificate was read for the first time in favour of Mr. Eric William Campbell, 97, Eaton Square, S.W.

A Ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Arthur Amos, B.A.; Albert Edward Andrews; John George Baxter; Francis George Belton; Edward Shipley Hewett Edwards Brettell-Vanhan; Thomas Walter Firth Clark; William Morris Colles, jun., B.Sc.; Miles Coupe; Roger Dodds; Sydney Dunstan; Bernard Scott Evans, B.Sc.; John Greig Ferrier; Frank Standish Findon, M.A., B.Sc.; Horace Finemore; Albert Gillies; Archibald Melville Glass, B.Sc.; Henry Isaac Gorman; Ernest Green; John Griffiths, B.Sc.; Samuel Ernest Groves; John Hawthorne; Arthur Lonsdale Hetherington, B.A.; James Henry Howgate, B.A.; Sydney A. Kay, D.Sc.; Leonard Gibbs Kilby, B.A.; William Henry Leek, B.A.; Ernest Isaac Lewis, B.A., B.Sc.; Peter Maguire; Ernest Robert Marle, B.Sc.; Francis Grimshaw Martin; Reginald Bruce Mangham; Edwin Morris; Alfred Mortimer, B.A.; Alfons O'Farrelly, M.A.; William Sarginson, B.Sc.; Frank Shedden, B.Sc.; Charles Stuart Shepherd; William Ewart Speight; Arthur Gordon Spencer, B.Sc.; Sydney Dockeray Stennitt, M.Sc.; Edmund Henry Stevens; Harold Blythen Stevens; Robert Reed Swann, B.Sc.; John William Taylor; George Devenish Thomas, B.Sc.; Arthur Walsh Titherley, D.Sc., Ph.D.; Francis Henry Wall.

Of the following papers, those marked * were read:—

*76. "Notes on Sodium Alum." By JOHN MELLO WADMORE.

The following experiment was made with the object of gaining information with regard to sodium alum, the existence of which was affirmed by Zellner in 1816, and subsequently by Augé (*Comptes Rendus*, 1890, cx., 1139), but denied by Ostwald ("Principles of Inorganic Chemistry," English edition, 1902, 556).

By mixing, in solution, quantities of sodium and aluminium sulphates in the proportion of their respective formula weights, a substance was obtained, crystallising in octahedra and having the appearance of an alum; moreover, the analytical data agreed closely with the numbers calculated for sodium alum, $Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$.

The solubility of the compound was determined at various temperatures, and found to be considerable. Thus, 1 grm. of water at 10.6° dissolves 1.0711 grms. of the crystalline salt.

Attention is drawn to the fact that a hot concentrated solution, on cooling, deposits a pasty or oily substance which is slowly transformed into crystalline sodium alum. This paste may possibly be a homogeneous mixture of anhydrous, or partly hydrated, alum and water.

Finally, it is shown that, whilst sodium alum does not effloresce appreciably under ordinary conditions, it rapidly parts with about half its water of crystallisation at 50° , but a higher temperature is needed to dehydrate it completely.

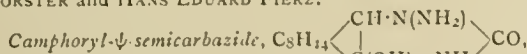
DISCUSSION.

Dr. MORGAN said that the author's results seemed to agree very closely with those already set forth in a recent patent (G. Dumont, D.R.-P. 141670; *Abstr.*, 1903, ii., 547), both observers having noticed the formation of the intermediate amorphous substance followed by that of a crystalline, non-efflorescent alum. Recently, in a preparation of β -benzoquinone, when a fairly concentrated solution of sodium dichromate was employed, he had noticed the pro-

duction of large well-defined crystals of sodium chrome alum, and he asked whether the author had made any experiments on the formation of this double salt.

Mr. WADMORE, in reply to a remark by Dr. Harden, said that there were several objections to the view that the paste might consist of anhydrous sodium sulphate, but admitted that the point required further investigation. As to the possible existence of sodium chrome alum, he had already made some experiments in this direction, and hoped shortly to be able to furnish definite information.

*77. "Camphoryl- ψ -semicarbazide." By MARTIN ONSLOW FORSTER and HANS EDUARD FIERZ.



obtained by reducing camphorylnitroso- ψ -carbamide with zinc dust in dilute acetic acid, dissolves readily in water, and crystallises from chloroform in minute white needles melting at 193° ; it has $[\alpha]_D^{20}$ 8.6° , and forms a definite nitrate, cuprintrate, and anhydride.

Condensation with certain aldehydes and ketones takes place very readily, and many of the products have high specific rotatory power; the following cases are typical:—

ψ -Semicarbazone.	M. p.	Solvent.	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
m-Nitrobenzaldehyde..	218°	Acetic acid	$+84^\circ$	301°
Acetone	217°	Chloroform	-188°	498°
Camphorquinone ..	234°	"	-314°	1172°
Benzaldehyde ..	223°	"	$+421^\circ$	1318°
Furfuraldehyde ..	222°	"	$+502^\circ$	1522°
Cinnamaldehyde..	219°	Ether	$+605^\circ$	2051°
Benzoquinone ..	197°	Acetone	-1051°	3310°

The camphoryl- ψ -semicarbazones are characterised by the tenacity with which they retain solvent of crystallisation; this property accounts for the profound influence on specific rotatory power exerted by various media. The cinnamylidene derivative, for example, has the following values in the solvents mentioned:—

Solvent.	$[\alpha]_D^{20}$.
Ether	$+605^\circ$
Chloroform ..	527°
Phenetole ..	451°
Bromobenzene ..	438°
Carbon disulphide ..	331°
Nitromethane ..	307°
Acetone	162°
Alcohol	107°
Acetic acid ..	96°
Pyridine	-54°

Similarly, the benzoquinone derivative has $[\alpha]_D^{20} - 1067^\circ$ in chloroform and $[\alpha]_D^{20} - 545^\circ$ in alcohol.

DISCUSSION.

Mr. W. ROBERTSON pointed out that the influence of the unsaturated linking on the rotation of optically active compounds was apt to be misinterpreted. The increase due to such a linking depends also on the position of the ethylenic bond; for example, Rupe has shown that menthyl caproate and menthyl hydrosorbate have almost identical specific rotatory power, although one is saturated and the other unsaturated. On the other hand, if the linking is close to the asymmetric complex or to a phenyl group, the change in rotation is very marked.

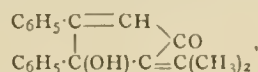
The PRESIDENT asked whether the compounds referred to by Dr. Forster as retaining their solvent of crystallisation with such obstinacy could be made to part with this attached solvent by heating, or whether they decomposed under this treatment. He congratulated the authors on having made what promised to be a most valuable addition to the agents available for the resolution of racemic neutral compounds such as aldehydes and ketones. The possible resolution of camphoryl- ψ -semicarbazide itself, referred to by Dr. Forster, had occurred to him also during the

reading of the paper, and he suggested that some naturally occurring unsaturated open-chain aldehyde possessed of optical activity, such as citronellal, might be found to answer the authors' requirements.

In reply to the President, Dr. FORSTER mentioned that the solvent of crystallisation is usually removed on prolonged exposure to a temperature approaching 100° without alteration on the part of the substances; attempts would be made to resolve the *pseudo*-semicarbazide on the lines suggested. He agreed with Mr. Robertson that the position of the unsaturated linking has influence on the rotation, but the series under consideration does not illustrate this point so clearly as Rupe's.

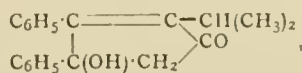
*78. "Some Derivatives of Anhydrazetonebenzil." By FRANCIS ROBERT JAPP and JOSEPH KNOX.

The condensation of benzil with unsaturated ketones has not hitherto been studied. The authors find that benzil interacts with methyl isobutenyl ketone, $CH_3 \cdot CO \cdot CH : C(CH_3)_2$, under the influence of potassium hydroxide to yield β -isopropylideneanhydrazetonebenzil,—

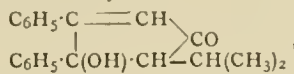


slender yellow needles, m. p. 205.5° .

With the corresponding saturated ketone, methyl isobutyl ketone, on the other hand, benzil condenses to form a mixture of α -isopropylanhydrazetonebenzil,—



six-sided prisms or slender needles, m. p. 142° , and β -isopropylanhydrazetonebenzil,—

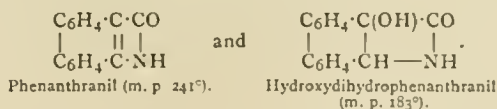


flat needles, m. p. 161.5° .

*79. "The Dihydrocyanides of Benzil and Phenanthraquinone." (Second Notice). By FRANCIS ROBERT JAPP and JOSEPH KNOX.

The authors find that when benzildihydrocyanide is treated with cold concentrated sulphuric acid, it yields diphenylacetamide, $(C_6H_5)_2CH \cdot CO \cdot NH_2$, m. p. $167.5-168^\circ$.

Japp and Miller (*Trans.*, 1887, li., 33) obtained, by the action of fuming hydrochloric acid on acicular phenanthraquinonedihydrocyanide, two compounds: $C_{15}H_9ON$ (m. p. 241°) and $C_{15}H_{11}O_2N$ (m. p. 183°). The present authors, from a study of the reactions of these compounds, assign to them the following constitutions:—



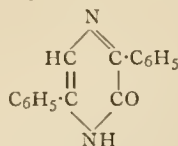
Both compounds are capable of interacting also in the tautomeric form, and it is at present impossible to say whether the free substances are lactams, as here represented, or the corresponding lactims.

*80. "A Condensation Product of Mandelonitrile." By FRANCIS ROBERT JAPP and JOSEPH KNOX.

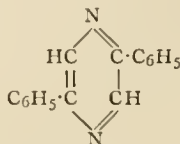
By saturating a solution of mandelonitrile in absolute ether with hydrogen chloride, Minovici (*Ber.*, 1899, xxxii., 2206) obtained a compound, $C_{16}H_{12}ON_2$, for which he gives the melting-point $200-203^\circ$.

The authors show that this compound is identical with a substance melting at $196-197^\circ$ previously obtained by Japp and Miller (*Trans.*, 1887, li., 29) by the action of hydrogen chloride on a solution of benzil in alcoholic hydrocyanic acid. They confirm the melting-point given

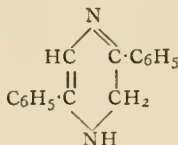
by Japp and Miller, and regard the compound as 3-*keto*-2 : 5-*diphenyl*-3 : 4-*dihydro*-1 : 4-*diazine*,—



By distillation with zinc dust, it yields 2 : 5-*diphenyl*-1 : 4-*diazine*,—



(m. p. 194—195°), whilst by heating with hydriodic acid and red phosphorus it is reduced to 2 : 5-*diphenyl*-3 : 4-*dihydro*-1 : 4-*diazine*,—



(m. p. 162—163°).

*81. "Action of Hydrazine on Unsaturated γ -Diketones." By FRANCIS ROBERT JAPP and JAMES WOOD.

C. Paal and Heinrich Schulze (*Ber.*, 1900, xxxiii., 3796) have shown that the *cis*- and *trans*-forms of *s*-dibenzoyl-ethylene, $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$, may be readily distinguished from one another by the greater ease with which the *cis*-form interacts with hydrazine to form a 1 : 2-*diazine*.

The present authors have employed this reaction to ascertain the configurations of some analogous unsaturated γ -diketones :— α -8-Dibenzoylstyrene, dibenzoylstilbene, and α -benzoyl-8-trimethacetylstyrene. One result has been to confirm the configurations assigned to the different modifications of the two former compounds by Japp and Klingemann (*Trans.*, 1890, lvii., 667), namely,—

	<i>cis</i> -Form.	<i>trans</i> -Form.
α -3-Dibenzoylstyrene ..	M. p. 129°	M. p. 197—198°
Dibenzoylstilbene ..	" 220°	" 232°

The *trans*-forms do not interact with hydrazine.

The only known form of α -benzoyl-3-trimethacetylstyrene (m. p. 115°) has the *cis*-configuration.

82. "The Synthesis of Substances allied to Adrenaline." By HENRY DRYSDALE DAKIN.

An account has recently appeared of the production of some compounds allied to adrenaline (D.R.-P. 157300; *Chem. Centr.*, 1905, i., 315), which have also been independently prepared by the author (*Proc. Physiol. Soc.*, 1905).

Methylaminoacetyl catechol,—



which is obtained by the action of methylamine on chloroacetyl catechol (Stolz, *Ber.*, 1904, xxxvii., 4149), is crystalline and melts at 232°; it forms soluble crystalline salts which are perfectly stable. The solution of the salts are very faintly acid, and the base is precipitated by sodium acetate. The base forms finely crystalline derivatives with phenylhydrazine acetate and with sodium-hydrogen sulphite.

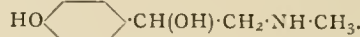
Natural adrenaline is generally assumed to be a secondary alcohol, whilst the above synthetical base is to be regarded as the corresponding ketone. On electrolytic reduction of the ketone or its bisulphite compound, a base is obtained which is probably not identical with racemic adrenaline.

This product forms deliquescent crystalline salts (for example, the hydrochloride and oxalate), the solutions of which are practically neutral. The free base is not precipitated from a solution of its salts by sodium acetate. The hydrochloride gives a precipitate with potassium ferrocyanide on boiling, and shows the usual colour reactions of catechol derivatives; it is unstable in hot aqueous solution, and is very readily decomposed by alkali even in the cold with evolution of methylamine. It has some physiological properties which are closely allied to those of adrenaline.

On addition of ammonia in slight excess to solutions of the salts, the free base is precipitated as a white, amorphous precipitate which is very sparingly soluble in most neutral solvents. The base may be kept for some little time suspended in water, but it is extremely unstable when dry, passing rapidly into a brown, insoluble substance with much less pronounced basic properties. This change may be analogous to that observed in the case of *o*-aminoacetophenone. Owing to experimental difficulties, satisfactory analytical data and molecular weight determinations have not yet been obtained.

The preparation of a base which is probably identical with the substance just described is given in the above-mentioned German patent; this product is obtained by acting on methylaminoacetyl catechol sulphate with aluminium shavings in the presence of mercuric sulphate, and it is assumed to have the following constitution :—

HO



If this is correct, the formula for natural adrenaline will require modification, but the author is of opinion that the available evidence is insufficient to determine whether the synthetical base is a secondary alcohol or whether it possesses another of several possible alternative structures.

Homologous bases of similar chemical and physiological properties have been obtained by the electrolytic reduction of ketonic bases obtained by the action of various amines on chloroacetyl catechol.

3. "Methylation of *p*-Aminobenzoic Acid by means of Methyl Sulphate." (Preliminary Note). By JOHN JOHNSTON.

By means of methyl sulphate, a practically quantitative yield of *p*-methylaminobenzoic acid may be obtained from *p*-aminobenzoic acid in presence of water. This compound is identical with that obtained by the action of methyl iodide on *p*-aminobenzoic acid, and melts at 144—145°. The melting-point of the acid prepared by Houben (*Ber.*, 1904, xxxvii., 3978) is given as 228—229°, and the melting-point of the acid prepared by Jaffé (*Ber.*, 1905, xxxviii., 1208) is given as 155—156°. Methyl *p*-methylaminobenzoate was prepared, and melts at 75—76°.

p-Dimethylaminobenzoic acid was prepared by the further action of methyl sulphate on the monomethyl derivative; it melts at 235—236°, and is identical with the product prepared by Michler (*Ber.*, 1876, ix., 401).

The process of methylation cannot be carried further by means of methyl sulphate in aqueous solution, the best method for the preparation of the trimethyl derivative being that described by Michael and Wing (*Am. Chem. Journ.*, 1887, vii., 195).

84. "The Atomic Weight of Nitrogen." (Preliminary Notice). By ROBERT WHYTLOW GRAY.

Many workers have pointed out that the atomic weight of nitrogen deduced by means of Avogadro's law from the relative densities of the pure gas and oxygen lies very near to the number 14.000 (Leduc, *Ann. Chim. Phys.*, 1898, [vii., xv., 5]).

When the two gases are compared under conditions in which this law may be considered to be strictly correct, the maximum value obtained lies below 14.010 (Guye, *Comptes Rendus*, 1904, cxxxviii., 1213; Rayleigh, *Phil. Trans.*, 1905, A cciv., 351).

The value 13.990 derived in a similar manner from nitrous oxide is also very close to these (Guye and Pintza, *Comptes Rendus*, 1904, cxxxix., 677).

The researches of Stas, however, lead to a totally different number, namely, 14.055, and the two sets of experimental results, if accepted, lead to the conclusion that either (1) the law of Avogadro is not true for gases containing nitrogen, or (2) the relative weight of the atoms of nitrogen and oxygen is not a constant.

To throw light on this point, a careful study has been made of nitric oxide, and the atomic weight of nitrogen has been deduced—(1) from the relative densities and compressibilities of nitric oxide and oxygen, (2) from the decomposition of nitric oxide by means of finely divided nickel.

In an earlier notice (*Proc.*, 1903, xix., 66) the weight of a litre of nitric oxide was stated to be 1.3402 grms. under normal conditions (lat. Paris). Since then, a much more elaborate purification of the condensed gas has been carried out in order to free it absolutely from the last trace of nitrogen, and the mean of 10 new experiments gave 1.3406 grms. for the weight of a litre at 0° and 760 m.m. (lat. Paris).

On correction by means of Berthelot's formula, 30.005 was obtained for the molecular weight of the gas, and hence the value 14.005 for the atomic weight of nitrogen.

The accurate analysis of nitric oxide proved a matter of difficulty; iron wire absorbed only slowly all the oxygen, and yielded traces of a gas condensable in liquid air which was probably cyanogen. With copper, the reaction was incomplete. Finally, it was found that the decomposition by means of finely divided nickel, discovered by Sabatier and Senderens (*Comptes Rendus*, 1892, cxiv., 1429), was an absolute one, and capable of being carried out with great accuracy. Before an experiment, the nickel was heated to bright redness in a vacuum to expel hydrogen and traces of moisture.

The nitric oxide was decomposed in the same bulb in which it was weighed, and the nitrogen was afterwards absorbed in a bulb containing charcoal, and cooled in liquid air. In this way, a complete analysis of the gas was made. The nickel oxide was found to contain traces of nitrogen, which were only expelled after heating to redness in a vacuum for a considerable time.

Six experiments were made, and the mean value for the atomic weight of nitrogen was found to be 14.006. This number is possibly a little too low, and more analyses are in progress.

85. "The Methylation of Gallotannic Acid." By OTTO ROSENHEIM.

The re-discovery of the optical activity of gallotannic acid rendered untenable the generally accepted formula for digallic acid put forward by Schiff (compare Rosenheim and Schidrowitz, *Trans.*, 1898, lxxiii., 878 and 885, and *Proc.*, 1899, xiv., 67), as this configuration does not contain an asymmetric carbon atom. It was thought that the study of the methylation products of this substance and their subsequent hydrolysis might provide a clue to its constitution. In view of the recent publication of Herzig and Tscherne (*Ber.*, 1905, xxxviii., 989), and as the author of the present communication is unable to continue the work, a short statement of the results already obtained seems justified.

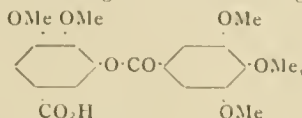
It was found that methyl groups could be introduced into the gallotannic acid molecule with the greatest ease by means of methyl sulphate. In alkaline solution, the reaction takes place in the cold, and a white amorphous substance is obtained, the yield being about 100 per cent of the gallotannic acid. The product may be purified by pouring its alcohol or acetone solution into water; it begins to melt at 95–98°, and is decomposed at a higher temperature, giving off carbon dioxide. It is insoluble in water, easily soluble in acetone, pyridine, or benzene, and resembles the parent substance in being dextrorotatory; a 2 per cent solution in acetone shows a rotation of 20° in a

100 m.m. tube. The analytical data indicate the formula $C_{10}H_{20}O_9$, according to which the substance is a pentamethylgallotannic acid, but owing to the amorphous nature of the substance its purity cannot, as yet, be guaranteed, and the numbers obtained are only approximate.

The compound obtained by Herzig and Tscherne, by means of diazomethane, gave numbers agreeing with the formula $C_{25}H_{10}O_7(O\cdot CH_3)_8$ or $C_{24}H_8O_7(O\cdot CH_3)_8$.

From the products of acid hydrolysis, two optically inactive substances are isolated, which are both soluble in ether, and may be separated by fractional crystallisation from water. The less soluble substance crystallises in long needles (m. p. 161°), and was recognised as trimethylgallic acid, whilst the more soluble compound, which was obtained in small acicular crystals (m. p. 187°), was identified with the dimethylgallic acid prepared by Herzig and Pollak (*Monatsh.*, 1902, xxiii., 700).

Assuming the validity of the old gallotannic acid formula, these results seem to agree with the following constitution:



which again, however, does not account for the optical activity of the substance.

86. "The Interaction of Hydrogen Sulphide and Sulphur Dioxide." By WILLIAM ROBERT LANG and CHARLES MACDONALD CARSON.

When hydrogen sulphide is passed into an aqueous solution of sulphur dioxide for several periods of from two to three hours on successive days, a milky solution is obtained which is termed Wackenroder's solution (Wackenroder, "On Pentathionic Acid," *Arch. Pharm.*, 1846, xlviii., 272, 140; Berzelius, *Jahresbericht*, 1847, xxvii., 36). This has been investigated by Debus (*Trans.*, 1888, liii., 278), who proved the presence therein of sulphur, and sulphuric, trithionic, tetrathionic, and pentathionic acids, and probably hexathionic acid. The salts of these acids were examined by Hertlein (*Zeit. Phys. Chem.*, 1896, xix., 287), who described methods for their separation and their physical properties. The explanation given by Debus for the formation of the polythionic acids is that tetrathionic acid is a direct product of the reaction of hydrogen sulphide on sulphurous acid, and that the other acids are formed from it by various subsequent reactions.

In order to investigate this, the reaction was effected, not in solution, but in the presence of a very little moisture, without which the gases do not interact. A large flask was surrounded with snow, a little moisture blown in, and the two gases then passed in at about equal rates for from two to three hours. A heavy yellow deposit, formed in the body of the flask, but not in the neck, was probably due to condensation of water having taken place only on the colder portions of the glass. This yellow material resembled ordinary sulphur, was dry to the touch, and quite brittle. On treatment with cold water, a milky liquid was obtained, and the substance became stringy; this product, when boiled with water, was rendered soft and elastic.

Deposits formed by the above methods at different times, on being heated to 100° for an hour, lost from 25–30 per cent by weight, and on estimating the sulphur compounds contained in them (as sulphuric acid) the amount never exceeded 1 per cent. Weighed quantities of the yellow material were allowed to remain in both open and closed tubes for several days at temperatures below 0°, but no change was noticeable in any case. When heated at 100°, the same loss of weight was observed as before; the presence of hydrogen sulphide could in no case be detected. Since the residue, after heating, contained more than 99 per cent of free sulphur, it may be concluded that the polythionic acids were present in extremely small amounts.

Several quantities of the yellow material were next placed in stoppered bottles at the temperature of the room.

After one day, the sulphur had become pliable and elastic, and was covered with an oily liquid having an acid reaction, while a strong odour of sulphur dioxide was perceptible on removing the stoppers. The amount of this liquid seemed to increase after the second day, and this was proved to be the case on estimating the sulphuric acid present in quantities which had stood for one and two days respectively, and which had afterwards been heated at 100° . This liquid was then obtained in larger quantities, and was found to have a sp. gr. usually above 1.35, and to correspond with what is commonly called pentathionic acid, and which Debus showed to be a mixture of polythionic acids. Around the neck of the bottles, while below 0° , colourless crystals had formed; these were in such small amounts that their composition was not determined, although, on warming, they gave off sulphur dioxide, and left a deposit of sulphur.

It would appear from the above experiments that the action of gaseous hydrogen sulphide on gaseous sulphur dioxide produces first sulphur and water, according to the equation $2\text{H}_2\text{S} + \text{SO}_2 = \text{S}_3 + 2\text{H}_2\text{O}$, with sulphur dioxide present in the sulphur in considerable quantities. The last two substances slowly interact at comparatively higher temperatures, giving rise to polythionic acids.

An attempt was made to investigate the action of anhydrous liquid hydrogen sulphide on liquid sulphur dioxide, but the drying of the gases was probably not thorough enough. About 5 c.c. of liquid hydrogen sulphide were collected in a thick-walled glass tube surrounded by a freezing mixture, dry sulphur dioxide passed in until the volume of the mixed liquids measured some 15 c.c., and the tube then sealed at the blowpipe. A slight yellow deposit was formed where the tube was sealed. After one day, a thin yellow film had formed at the upper part of the tube which gradually increased, and when the tube was opened after one week there was found in the bottom a solid lump of sulphur covered by a clear liquid. This liquid, when allowed to evaporate, gave off sulphur dioxide, and left a small quantity of water containing dissolved sulphur dioxide.

Methods for the detection and estimation of the different polythionic acids which will, it is hoped, enable the composition of the oily mixture of acids to be accurately determined are at present being investigated.

87. "The Formula of Cyanomaclurin." By ARTHUR GEORGE PERKIN.

Although cyanomaclurin bears a close relationship to catechin, $\text{C}_{15}\text{H}_{14}\text{O}_6$, and analyses of its derivatives were in harmony with the suggestion that it was isomeric with this substance (*Proc.*, 1904, xx., 171), it was now found by exhaustive analysis of the compound itself purified in various ways that the formula $\text{C}_{15}\text{H}_{12}\text{O}_6$ is to be preferred. Consequently its derivatives are to be represented as follows:—Acetyl cyanomaclurin, $\text{C}_{15}\text{H}_7\text{O}_6(\text{C}_2\text{H}_3\text{O})_5$; benzoylcyanomaclurin, $\text{C}_{15}\text{H}_7\text{O}_6(\text{C}_7\text{H}_5\text{O})_5$; benzenecyanomaclurin, $\text{C}_{15}\text{H}_{10}\text{O}_6(\text{C}_6\text{H}_5\text{N}_2)_2$; and acetylbenzenecyanomaclurin, $\text{C}_{15}\text{H}_7\text{O}_6(\text{C}_6\text{H}_5\text{N}_2)_2(\text{C}_2\text{H}_3\text{O})_3$.

Royal Institution.—On Saturday next, May 20, at 3 o'clock, Dr. J. G. Frazer will deliver the first of a course of two lectures on "The Evolution of the Kingship in Early Society"; on Tuesday, May 23, at 5 o'clock, the Rev. Henry G. Woods commences a course of three lectures on "Velazquez"; and on Thursday, May 25, at the same hour, Professor J. A. Fleming delivers the first of three lectures on "Electromagnetic Waves." These are the Tyndall Lectures. On Saturday, June 3, at 3 o'clock, Mr. A. H. Savage Landor begins a course of two lectures on "Exploration in the Philippines." The Friday Evening Discourse on May 26 will be delivered by Professor J. W. Brühl on "The Development of Spectro-chemistry," on June 2 by Mr. George Henschel on "Personal Recollections of Johannes Brahms," and on June 9 by Sir William H. White on "Submarine Navigation."

NOTICES OF BOOKS.

Zur Bildung der Ozeanischen Salzablagerungen. ("The Formation of Oceanic Salt Deposits"). By J. H. VAN 'T HOFF. Braunschweig: Friedrich Vieweg und Sohn. 1905.

THIS volume gives a summary of the results of the investigation which Profs. van't Hoff and Meyerhoffer have for some years been prosecuting on the subject of the formation of oceanic salt deposits. A short sketch of the same subject, which was given in the author's lecture before the University of Chicago in 1901, as one of a course on "Physical Chemistry in the Service of the Sciences," was sufficient to arouse the interest of both geologists and chemists, and this is fully maintained in the more detailed account of the investigation. The research is limited to the consideration of the problem of the formation of the beds of the most important salts only, *i.e.*, sodium chloride, magnesium chloride and sulphate, and potassium chloride and sulphate, reserving the calcium salts and borates for treatment in a subsequent volume. The author explains the experimental methods he has adopted in examining the process of crystallisation of solutions of the above mentioned salts when variations are made in the temperature, pressure, and time, and then proceeds to the application of the general principles thus discovered. The details of the processes are much simplified by means of the charts which represent graphically the course of crystallisation, and enable it to be traced through the formation of the chief salt beds. The resourcefulness and ingenuity displayed by the author in working out the important problems which are discussed in the book, especially as regards experimental procedure, will command the admiration of all students of physical chemistry and oceanography.

Chemische Technologie und Analyse der Ole, Fette, und Wachse. ("The Chemical Technology and Analysis of Oils, Fats, and Waxes"). By Dr. J. LEWKOWITSCH. Braunschweig: Friedrich Vieweg und Sohn. 1905.

THE German version of Dr. Lewkowitsch's standard work, while following the third English edition fairly closely, is by no means a literal translation from it, and in many places it has been considerably abridged, so that on the whole the English version will be found preferable for the use of those who are conversant with both languages. In the German numerical and other examples are frequently omitted, and in some places alternative methods of quantitative determination are cut out; the appendices are included in the text, and various other alterations are made in the arrangement of the matter. The preface to the third English edition is included, and the division of the subject into the analytical portion, dealt with in the first volume, and the technology of oils and fats, to which the second volume is devoted, is preserved.

CORRESPONDENCE.

COLOURATION OF GLASS BY RADIATION.

To the Editor of the Chemical News.

SIR,—In connection with your article on the "Colouration of Glass by Solar Radiation" (*CHEMICAL NEWS*, xci., 73), I would say that there is a marked instance of such colouration in Boston, Mass., U.S.A. Many of the houses on the Back Bay have in their windows glass that was imported from England at a very early period. This glass has turned to colours of various shades: pink to violet and almost blue. In these cases high altitude could have had nothing to do with the matter. The houses face east. I have seen many illustrations of the effect of sunlight on ordinary window glass. Names printed on glass by means of black paper, and the glass exposed to the sun for short

periods, will show out plainly on removing the paper. I have seen a regular gradation of colour by taking a piece of glass and progressively covering it with black paper, allowing each period to remain exposed a month longer than the preceding period. Such instances may be well known to you, but I thought these might be of interest.—I am, &c.,

WILSON H. LOW.

The Cudahy Packing Co.,
South Omaha, Neb., April 20, 1905.

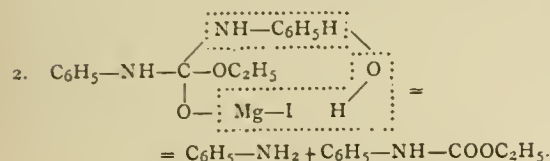
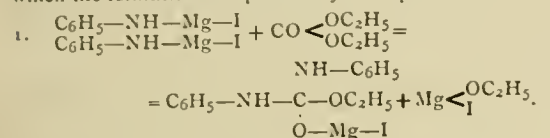
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxl., No. 16, April 17, 1905.

Luminescence of Arsenious Acid.—M. Guinchant.—The crystallo-luminescence of arsenious acid, investigated by Rose, takes place in all the varieties of the acid, and only depends on the concentration of the acid in HCl. The luminescence is evidently due to a chemical phenomenon corresponding to the reversible reaction $\text{As}_2\text{O}_3 + 6\text{HCl} \rightleftharpoons 3\text{H}_2\text{O} + 2\text{AsCl}_3$.

Method of Formation of certain Mono-substituted Derivatives of Urethane.—F. Bodroux.—When small portions of neutral ethyl carbonate are dropped into ether holding—either in solution or suspension—the magnesium derivative of a primary aromatic amine, a rapid reaction takes place, which ceases in a few seconds. With aniline the action results in the production of phenylurethane, of which the formation is expressed by the equations—



No. 17, April 24, 1905.

This number contains no chemical matter.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxviii., No. 3, 1905.

Tungsten Hexafluoride.—Otto Ruff and Fritz Eisner.—The authors have found that they can prepare this substance, which has never yet been isolated, by the action of anhydrous hydrofluoric acid on anhydrous tungsten hexachloride. The anhydrous acid they prepared by heating absolutely dry potassium hydrogen fluoride in a platinum retort. After preliminary experiments, which showed that the product of the reaction of tungsten hexachloride with anhydrous hydrofluoric acid is a substance which is gaseous at ordinary temperatures, a strong walled iron bomb lined with copper was used for its preparation. In this were placed 8 grms. of tungsten hexachloride, and it was cooled to -70° in an alcohol-carbonic acid mixture; then 12 grms. of anhydrous hydrofluoric acid were distilled in, the air in the bulb was replaced by carbon dioxide; the bomb was then closed, and the cooling mixture removed. After

keeping the bomb for twenty-four hours at the ordinary temperature it was again cooled to -70° , and opened. A considerable quantity of hydrochloric acid escaped, together with a little HF, and the new compound, the presence of which could be demonstrated by the blue deposit of lower oxides formed on a silver coin which was held in the vapour. In order to retain the HF, into the bomb was inserted a copper tube about 30 c.m. long and $1\frac{1}{2}$ c.m. diameter, filled with sodium fluoride; the tungsten compound escaping through this was condensed in a glass apparatus cooled to -70° . At the same time a current of carbon dioxide was led into the bomb to drive the gases into the vessel. Unfortunately only very small quantities of the tungsten compound condensed, most of it having remained in the sodium fluoride tube, forming a stable double compound there; this compound did not give up the tungsten hexafluoride on heating. Finally, it was found that if the sodium fluoride was replaced by liquid titanium tetrachloride absorbed by charcoal, the hydrofluoric acid forms a tetrafluoride with it, while the volatile tungsten compound has no action upon it. The yield of tungsten hexafluoride is only about 20 per cent of the theoretical yield, partly because the copper vessel is not very resistant to WF_6 and HF, and gives rise to the tungsten compounds, and partly because a temperature of -70° is somewhat too high, though it is found impossible to work at a lower temperature on account of the difficulty of separating the tungsten hexafluoride from the hydrochloric acid. The gaseous hexafluoride rapidly attacks glass, some SiF_4 being formed, and probably oxyfluorides of tungsten also. For this reason the interior of all glass vessels used in its preparation must be coated with paraffin. The solid sublimate forming on the walls of the paraffined glass vessel was found to contain hydrochloric acid and a non-volatile tungsten compound. The determination of the molecular weight of WF_6 gives the value 286.6. It is a colourless gas at the ordinary temperature, ten times as heavy as air, and is thus the heaviest gas known. At some degrees above 0° and atmospheric pressures it vapourises without previously fusing. Gaseous WF_6 fumes in air, forming bluish white vapours. It is easily and completely absorbed by alkalis, and forms double compounds with alkaline fluorides. It decomposes with water, yellow tungstic acid hydrate separating out. The gas rapidly attacks metals, such as iron, zinc, tin, nickel, &c., especially if it contains HF, covering them with a blue or grey deposit of tungsten compounds. Molybdenum pentachloride reacts with anhydrous HF in the same way as WCl_6 , forming a gaseous fluoride resembling WF_6 in properties, but still more difficult to purify in copper or glass vessels.

Action of Persulphates on Haloid Salts.—M. Dittrich and H. Bollenbach.—If potassium chloride is precipitated with slightly acid silver nitrate solution in presence of a 10 per cent solution of ammonium persulphate, and the precipitate weighed, the percentage of chlorine obtained is found to be too low, which shows that some of the chlorine has either escaped or else formed higher oxygen compounds. If aqueous sulphurous acid is added to the filtrate and the solution warmed on the water-bath, more nitric acid being added to dissolve the silver sulphite which separates out, a further precipitate of silver chloride is obtained. If the chlorine in this is calculated and added to the amount previously obtained, the sum of the two quantities is found to agree with the chlorine in the potassium chloride used. Thus, by the action of a persulphate in acid solution upon silver chloride only silver chlorate is formed, for if perchlorate were produced it would not be reduced by sulphurous acid. The quantity of chlorate formed depends upon the length of time during which the action continues. Similarly with bromides small quantities of bromate are formed, while iodides are readily completely transformed into iodates. No perchlorates or periodates are formed.

New Method of Analysis of Perchlorates.—M. Dittrich and H. Bollenbach.—To determine sodium

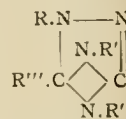
perchlorate in commercial saltpetre, sodium or potassium nitrite can very conveniently be used to reduce to chloride, the following reaction taking place:— $\text{KClO}_4 + 4\text{KNO}_2 = \text{KCl} + 4\text{KNO}_3$. A layer of pure, finely powdered sodium nitrite is spread over the bottom of a platinum or nickel dish, and in the middle is placed a weighed quantity of the substance to be examined, care being taken that none is left on the sides of the dish. It is then covered with a layer of nitrite (using about 6 grms. of KNO_2 in all), and gently warmed. It is kept in a state of fusion at the lowest possible temperature for half-an-hour, then cooled, and taken up with warm water. Silver nitrate is added, and the solution is made strongly acid with nitric acid, and the HNO_2 driven off on the water-bath. The AgCl is then determined in the usual way.

New Method of Determining Tungsten.—G. v. Knorre.—If benzidine chlorhydrate is added to a solution of sodium paratungstate, a white amorphous precipitate of benzidine tungstate is formed. When excess of benzidine chlorhydrate is used the precipitation is quantitative. The precipitate is difficult to filter unless the liquid is heated to boiling, but as benzidine tungstate is not quite insoluble in hot water, it must be allowed to become perfectly cold before filtration. The precipitate is best washed with a dilute solution of benzidine chlorhydrate. It may also be filtered easily without boiling if some dilute sulphuric acid or alkali sulphate is previously added to the tungstate solution, and this method is generally to be preferred as being more rapid. When tungstic acid is to be determined in a solution which contains sodium carbonate as well as sodium tungstate, the necessarily cautious addition of acid tends to cause the formation of metatungstic acid which is not completely converted into the insoluble modification by once evaporating to dryness, so that the filtrate from the tungstic acid almost always contains tungsten. It is then best to evaporate with excess of sulphuric acid and to heat until white fumes of sulphuric acid escape. In the analysis of tungsten steel by this method, since ferric salts oxidise benzidine salts, the iron must first be reduced to the ferrous state by means of sulphuretted hydrogen; it is then found that the tungsten result comes out rather higher than when the usual method is adopted, but the research has not yet been concluded.

Salts of Zirconium.—Arthur Rosenheim and Paul Frank.—Zirconium, which is placed between titanium and cerium in the periodic system, is an extremely feeble electropositive element. Hence neutral salts of the tetravalent cation Zr^{++} are unstable in dissociating media; from such solvents salts of divalent zirconyl cation are obtained, e.g., $\text{ZrOCl}_2 + 8\text{H}_2\text{O}$. All attempts to obtain a hydrate of zirconium tetrachloride by the action of strong alcoholic hydrochloric acid on zirconium hydroxide fail, since the addition of the least quantity of water always gives the above zirconyl chloride octohydrate. But in the solution in absolute alcohol zirconium tetrachloride must be present, because, as in the cases of thorium and titanium, on addition of chlorides of organic bases crystallised salts of a zirconium chloride and hydrochloric acid are obtained. Thus, with pyridine chloride a substance of the formula $(\text{C}_5\text{H}_5\text{N})_2\text{H}_2\text{ZrCl}_6$ is obtained. An analogous salt, $(\text{C}_5\text{H}_5\text{N})_2\text{H}_2\text{ZrBr}_6$, is also known, but it is very unstable, giving up hydrobromic acid in the air. Zirconium sulphate has the formula $\text{ZrO}(\text{SO}_4\text{H})_2$; if to an aqueous solution of this salt a solution of neutral potassium sulphate is added in the cold a crystalline precipitate separates out. This compound is very easily hydrolysed, and on standing in aqueous solution, or on warming, zirconium hydroxide or basic zirconium sulphate separates out. But if precipitated in the cold, rapidly filtered, and washed with alcohol and ether, a homogeneous crystalline compound is obtained. The composition of this is expressed by the formula $\text{Zr}_2\text{O}_3(\text{SO}_4\text{K})_2 \cdot 8\text{H}_2\text{O}$. The corresponding rubidium and caesium salts contain 15 and 11 molecules of water respectively. But on addition of sodium or ammonium sulphate to solution of zirconyl sulphate, analogous salts

are not obtained, but amorphous basic products. This is probably due to the great solubility of the sodium and ammonium sulphate zirconyl salts, so that before they can crystallise the zirconyl sulphuric acid complex begins to hydrolyse. If a concentrated solution of acid potassium sulphate is saturated when boiling with freshly precipitated zirconium oxide hydrate, from the strongly acid filtrate crystalline needles of a compound $\text{Zr}(\text{SO}_4\text{K})_4 \cdot 3\text{H}_2\text{O}$ separate out. The analogous sodium and ammonium salts may easily be prepared.

Gravimetric Determination of Nitric Acid.—M. Busch.—The endimino-dihydrotriazoles, which have the formula here shown and are prepared by the condensation of amino-guanidines with carboxylic acids, form a group of bases whose nitrates are marked by their insolubility in water, and they can thus be used to precipitate nitrate ions directly. The best base to employ for this purpose is the diphenyl-endanilo-dihydrotriazol, which is supplied by the firm of E. Merck, of Darmstadt. If five or six drops of a 10 per cent solution of this base in 5 per cent acetic acid are added to the nitrate solution acidified with dilute sulphuric acid (one drop), a voluminous white precipitate is obtained. If only one part of nitrate is present in 60,000 it may be detected by this test, though the crystals only become visible after the solution has stood for some hours. This refers to the temperature of the room; at 0° one part of nitrate in 80,000 is sufficient to give the precipitate. Unfortunately, some other acids form difficultly soluble salts with the same bases. Such are hydrobromic acid, which may be removed by means of HCl ; hydriodic acid, which is best oxidised by iodate, and the iodine removed in the usual way; nitrous acid, which is destroyed by hydrazine sulphate; and chromic acid, which is reduced by the same reagent. In performing quantitative determinations it is best to precipitate in hot solution, then to cool the liquid with ice-water, and wash with the least possible quantity of water, the use of a Neubauer crucible being preferable to filtering through paper. The precipitate may be dried at 110° . The same method may be employed for the quantitative determination of a nitrate in presence of a nitrite, but as the nitrite of the base is not quite insoluble in water the HNO_2 must first be removed. Hydrazine sulphate is the best agent for this purpose, as when it is used the nitrous acid forms practically no nitric acid. The substance containing nitrate and nitrite is taken up with a little water, and finely powdered hydrazine sulphate is slowly added to the solution. When no more nitrogen is evolved the liquid is heated to boiling, and treated as before with the diphenylendanilo-dihydrotriazol.



MEETINGS FOR THE WEEK.

- MONDAY, 22nd.—Society of Arts, 8. (Cantor Lecture). "Use of Electricity in Mines," by H. W. Ravenshaw, Assoc. M. Inst. C.E.
- TUESDAY, 23rd.—Royal Institution, 5. "Velazquez—The Young Velazquez," by the Rev. Henry G. Woods, D.D. Society of Arts, 4.30. "The Cape to Cairo Railway," by Sir Charles H. T. Metcalf, Bart., M. Inst. C.E.
- WEDNESDAY, 24th.—Society of Arts, 8. "Modern Lightning Conductors," by Killingworth Hedges, M. Inst. C.E.
- THURSDAY, 25th.—Royal Institution, 5. (The Tyndall Lectures). "Electromagnetic Waves," by Prof. J. A. Fleming, F.R.S., &c.
- FRIDAY, 26th.—Royal Institution, 9. "The Development of Spectrochemistry," by Prof. Julius Wilhelm Brühl, Ph.D. Physical, 3.30. (At the National Physical Laboratory). "The Specific Heat of Iron at High Temperatures," by Dr. Harker. "The Measurement of Small Inductances," by Mr. Campbell. "Two New Optical Benches," by Mr. Selby.
- SATURDAY, 27th.—Royal Institution, 3. "Evolution of the Kiogabip in Early Society," by James G. Frazer, D.C.L., LL.D., Litt.D.

THE CHEMICAL NEWS.

VOL. XCI., No. 2374.

A STUDY OF THE PROCESS OF NITRIFICATION WITH REFERENCE TO THE PURIFICATION OF SEWAGE.*

By HARRIETTE CHICK, D.Sc.

IN 1890-2 Winogradsky isolated from surface soil the two organisms which co-operate to produce natural nitrification, the nitrite producer which oxidises ammonia compounds to the nitrite stage only, and the nitrite producer which finishes the process but cannot act on ammonia, being, indeed, quite inhibited in its development by minutest traces of that substance. The most striking characteristic of these organisms is their repugnance to the presence of organic matter. Not only, in opposition to all the rest of the plant world, do they make no nutritive use of sugars, peptones, &c., but the presence of more than a trace of organic substance entirely inhibits their development.

It appeared, then, unlikely that the organisms which accomplish the oxidation of ammonia to nitric acid in industrial filter-beds, on to which quantities of organic sewage matters are continually poured, should be of the same nature as these isolated by Winogradsky.

A detailed study of this process was therefore undertaken, and chemical and bacteriological investigations of the working of model "contact" and "continuous" sewage-filters were made, both when the filters were mature and during the process of maturation. These researches were carried out in the Institutes of Hygiene in Vienna and Munich.

The model filters, 12 c.m. in diameter and 50 to 200 c.m. high, were filled with fine coke, and provided with side tubes at various levels, by which liquid from different strata could be drawn off.

The filters were kept working, supplied with liquid manure roughly filtered, for various times up to a year, and tables are given of the significant variations in the composition of the filtrate. The various compounds of nitrogen, free and saline ammonia, albuminoid ammonia, nitrites, nitrates, and total nitrogen were periodically estimated, and the oxidation of other elements than nitrogen (carbon, &c.), was also followed.

The filters, on being started, become spontaneously inoculated, and steadily mature to full efficiency, passing through definite stages more or less sharply separated. At first oxidation of carbon, &c., alone goes on, and ammonia passes through unchanged. In a month, oxidation of ammonia to nitrites begins, and soon becomes complete; then nitrates begin to appear in the effluent. After several months nitrates alone are being discharged.

The distribution of these stages in time is paralleled by their distribution in strata in the continuous filter. The oxidation of carbon almost monopolises the upper strata, and the oxidation to nitrites and nitrates tends to occur only in the lower strata. The disappearance of ammonia corresponds strictly, both in time and space distribution, with the appearance of oxidised nitrogen. Apparently the abundance of organic matter keeps the nitrifying organisms from invading the upper layers.

Both contact and continuous filters were working more efficiently than they do on the industrial scale; the continuous filters matured quickest and were more efficient, one of only 5-litre capacity oxidised 0.5 gm. nitrogen daily. A rise in temperature of a few degrees produces a distinct

acceleration of activity; a point that has practical applications.

Much fruitless labour was expended in attempting to isolate, by means of media containing organic matter, the essential organisms acting in these filters. Ultimately they were isolated by Winogradsky's pure saline media, and prove to differ only very slightly from the organisms isolated by him from soil. When this work was drawing to an end, Dr. Schultz-Schultzenstein published the successful isolation of both Winogradsky's organisms from coke filter-beds.

Various possible explanations of how the Winogradsky organisms manage to flourish in filter-beds rich in organic matter are considered.

An interesting symbiotic state was kept in cultivation for some time; this was a union of the nitrate organism with a specific non-nitrifying organism; the presence of the latter enabled the former to develop through several generations in organic media without loss of nitrifying power. When isolated from its consort the former showed the characteristic inhibition by such media.

The current theory of the action of filter-beds holds that ammonia compounds are physically absorbed by the solid porous material and retained until the bacteria have time to nitrify them. A precise investigation of a number of such solid substances was therefore instituted. It failed, however, to reveal any such power of absorbing ammonia salts.

Probably, then, no physical, but only a biological process is at work, and the disappearance of ammonia is directly and only due to its being nitrified as fast as it trickles down the filter. The constant trickling and the perfect aeration of the continuous filter provide very perfect biological conditions for the activity of such an organism. In efficiency the continuous filter surpasses the contact filter, and deserves more extended trial.

THE EFFECT OF PLANT GROWTH AND OF MANURES UPON THE SOIL: THE RETENTION OF BASES BY THE SOIL.*

By A. D. HALL, M.A., and N. H. J. MILLER, Ph.D.

THE investigation deals first with the variations in the amount of calcium carbonate—the only basic substance usually available in soils—in the experimental plots at Rothamsted. The soil of the Rothamsted Estate is naturally almost devoid of calcium carbonate, but owing to the practice of "chalking" (common in the eighteenth century) having been resorted to, the surface soil still contains about 3 per cent of calcium carbonate. Since samples of soil taken at various dates back to 1856 still exist, it has been possible to determine the annual rate of loss brought about by the removal of calcium carbonate as bi-carbonate in the water percolating through the soil.

In four of the fields which have been unmanured during a long period, the loss of calcium carbonate amounts to about 1000 lbs. per acre per annum. This rate of loss is much increased on some of the manured plots; the use of ammonium sulphate and chloride, as sources of nitrogen, causes an increased loss of calcium carbonate which is equivalent to the amount required to neutralise the acid of the salts applied. There is, however, no evidence of the loss of the second molecule of the calcium carbonate which would be required to form calcium nitrate on the nitrification of the ammonia.

When sodium nitrate is used as a manure the rate of removal of calcium carbonate is lower than on the unmanured plots. Farm-yard manure has also a similar conserving effect on the calcium carbonate in the soil. Evidence is also brought forward showing that many soils which are initially very poor in calcium carbonate, retain their

* Abstract of a Paper read before the Royal Society, May 11, 1905.

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fertility unimpaired for many years, and even show no decline in the small amount of base they contain, although nitrification is always going on, and requires a supply of base from the soil. Hence it is concluded that some agencies must exist which, under ordinary circumstances, restore base to the soil. Water cultures of wheat in a solution containing calcium nitrate and other neutral salts show that the plant withdraws more acid than base from the solution, leaving behind an alkaline residue in the state of bi-carbonate. A consideration of the analyses of the ash of field crops demonstrates that this restoration of base to the soil takes place normally, and in quantities of the same order as the amount of base which had been required for the nitrification of the nitrogen present in the plant.

Other experiments showed the presence in the soil of bacteria capable of converting into calcium carbonate the calcium oxalate which is the most abundant compound of calcium in plant residues. The authors consider that these two actions, both of which recreate calcium carbonate in the soil, are sufficient to account for the maintenance of a neutral condition in cultivated soils poor in calcium carbonate, a fact that has hitherto been difficult to understand in view of the continual drift on the soil bases brought about by the process of nitrification.

COLOURATION OF GLASS BY SOLAR RADIATION.

WE have received the following letter from Mr. EDWARD S. SIMPSON, B.E., Geological Survey Laboratory, Perth, Western Australia:—

"I have been much interested in your article in the *CHEMICAL NEWS* of February 17th (vol. xci., p. 72), on the purple colouration of glass by the sun's rays. This phenomenon is very frequent in Western Australia, both in Perth on the coast and inland on the Goldfields.

In the city of Perth (level 10 to 60 feet) the glass prisms used in the foot-paths to light underground offices are often in a year or two turned into quite a deep amethyst colour.

On the Coolgardie and adjacent goldfields (level 1000 to 1500 feet), which prior to 1893 were uninhabited desert, the ground is strewn thickly in places with fragments of tumblers, &c., turned all shades of purple. Where a fragment is partly buried under the soil the exposed part is a much deeper colour than the unexposed. It would appear therefore to be due to the sun's rays rather than emanations from the ground. If samples of glass so affected would interest you, I shall be very pleased to try and collect some for you.

The sky is practically cloudless all the year round on the Goldfields, and all through the summer here in Perth.—I am, &c.

EDWARD S. SIMPSON.

N.B.—Max. noon altitude of sun at Perth, $81^{\circ} 30'$.
Min. " " " $34^{\circ} 37'$.

Determination of Acids Combined with Aluminium.
—Oto Schmatolla.—If aluminium sulphate solution is titrated with normal alkali a considerable difference is found in the titrations, according as traces of carbonate are present or not. The author has found that it is best to use soda solution, always titrating when boiling, as the change in the indicator is then very sharp and distinct. In the case of neutral aluminium sulphate the change has been found to be always incomplete, but the reaction is perfectly constant, and the error may be corrected by increasing the number of cubic centimetres by $\frac{1}{110}$. With acetate, nitrate, and chloride of aluminium it is best to add excess of soda and titrate the excess.—*Berichte*, xxxviii., No. 4.

CHARACTERISTIC ABSORPTION PHENOMENON OF THE DIAMOND.

By B. WALTER.

SOME months ago I ordered from the diamond merchant, Herr E. Winter, of Hamburg, a three-sided diamond prism cut on all side surfaces; its surfaces were to be as nearly as possible plane, its edges as nearly as possible parallel, and its angle of refraction approximately 60° . The weight of the prism delivered to me was about $\frac{1}{2}$ carat (1 carat = 0.205 grm.), and it exhibited the desired properties beyond my expectations. The surfaces were so perfectly plane that in spite of their smallness they clearly reflected the cross threads in the focus of the objective of a Gauss' eye-piece. The measurement of the angles of refraction, moreover, gave $60^{\circ} 0' 40''$, $60^{\circ} 38' 25''$, and $59^{\circ} 21' 22''$, whence it followed also that the edges were sufficiently parallel, as the sum of the angles was nearly 180° . This, moreover, also resulted from the fact that the prism could be so adjusted upon the spectrometer that the mirror image of the horizontal thread in the eye-piece in the case of all three surfaces so nearly coincided with the thread itself that the deviations could be almost entirely ascribed to the eccentricity of the instrument.

I mention these facts because possibly this prism was the first of its kind, and thus it might be of interest to know what might be expected in the way of accuracy, even in so hard a material.

I now allowed a ray of sunlight to pass through this prism, which by the way was fitted for experiments on reflection colours, in such a way that it met the first surface perpendicularly, was then reflected in the interior on the second surface—on the outside of which was a layer of fuchsine—and then passed through the third surface almost perpendicularly; when I further caught this ray with the slit of a spectroscope, the spectrum of it—besides some phenomena in the orange, which were caused by the fuchsine layer, and which need not therefore be further discussed here—unexpectedly showed in the violet between Fraunhofer's lines G and h, a faint dark band α , which was not present in the normal sun spectrum. As this band for theoretical reasons could not be caused by reflection on the diamond fuchsine layer, I was led to suppose that it was an absorption band of the diamond itself, a conclusion which of course could be immediately confirmed by removing the fuchsine layer in the experimental procedure described above. The band α was still obtained unaltered in strength.

There occurred now the question whether the undoubted absorption of this one diamond was a characteristic property of solid crystallised carbon generally, or whether it was to be ascribed only to an accidental impurity of my special specimen. This could be most easily decided by submitting as many crystals as possible to an examination, which was rendered possible for me on a large scale by the kindness of the firm of diamond importers, Messrs. Bozenhardt and Co., of this place.

In these observations, which related chiefly to cut brilliants, but frequently also to uncut stones, I collected the sunlight coming from the heliostat by means of a powerful burning lens of focal length 20 c.m. on as smooth a surface of the crystal as possible—in the case of brilliants always on the smallest of the two surfaces which were cut parallel, collected the light emerging on the other side by means of a similar lens of focal length 40 c.m., and then caught it with the slit of the spectroscope. For the preparation of photographs the light was previously sent through a narrow slit, which, in order to obtain the greatest possible intensity, was placed a short distance behind the focus of the first lens. In addition to this the light, made almost parallel by means of the second lens, was sent through a monobromnaphthalene prism, and finally the sharp spectral image was thrown by a third lens of focal length 85 c.m. placed immediately behind the prism. Into this ordinary photographic plates were placed

with certain due precautions, and after a suitable time of exposure they were developed and fixed, also in the usual way.

The closer examination of as many different kinds of diamonds as possible—there were altogether about 50—at once showed that the absorption band α could not be either a peculiarity of solid crystallised carbon—for then the strength of the band would stand in a constant relation to the thickness of the crystals, which was by no means the case—nor, on the other hand, was it a case of an accidental impurity of that one crystal. For the band α was again found in by far the greatest number of stones I examined, and indeed without exception in all of the larger colourless crystals: thus, for example, in all white brilliants over 1 carat in weight. The intensity of the band differed in the different stones in quite an irregular manner, but always within fairly narrow limits.

The so-called "water" of the diamond, *i.e.* its colourlessness, does not seem to be injured by the presence of the absorption so long as it does not exceed a certain degree; for often stones which were pointed out to me as the finest specimens showed the band α considerably more strongly than other less valuable stones.

Also the locality which the mineral was found made no difference; for diamonds from Brazil behaved in exactly the same manner as several Cape diamonds, and even an East Indian uncut stone, which was entrusted to me through the kindness of Herr Gottsche from the mineralogical collection of the Natural History Museum of Hamburg, showed the band α of normal strength.

In the smaller colourless brilliants the absorption could not always be established—probably on account of the thinness of the absorbing layer; so that, for example, among 16 small brilliants of average weight $\frac{1}{4}$ carat, in one no absorption whatever was to be seen, in three or four a doubtful absorption appeared, and in the others a distinct absorption.

The examination of coloured crystals further showed that in the rarer and mostly smaller examples of reddish, greenish, or brownish colour, ordinarily only a faint absorption appeared, and, generally speaking, there was nothing to be seen of the band α ; on the contrary, the light yellow sorts occurring so frequently and also so often in larger crystals, showed the band α quite extraordinarily strongly.

In crystals of this sort the band α is accompanied also by other absorption phenomena, which seem to be due to the same cause, and hence deserve closer attention. Namely, besides the very strong band α , the middle of which lies at wave-length $\lambda = 415.5$, we see first of all at about $\lambda = 471$ an exceedingly faint somewhat broad absorption band δ . Moreover, the light yellow stones always show a fairly strong absorption in the ultimate violet and in the ultra-violet, which is divided by a clearly visible maximum brightness, occurring shortly before H, into two parts, β and γ . The absorption γ seems to extend over the whole of the ultra-violet, as far as it can be followed up, at any rate, with the glass apparatus used—about as far as N.

All the observations given in the preceding now show undoubtedly that the cause of the absorption α is to be sought in an impurity of the diamond, which is perhaps not without influence upon the origin of the crystal. To establish the nature of this impurity is the business of chemistry, but I may allow myself to make the following remarks on this point:—Our first thoughts naturally turn towards that group of metals whose compounds are recognised by giving absorption spectra with bands resembling lines, *i.e.*, to the group of the rare earths. But of the substances of this kind now known, only one—samarium—gives an absorption band ($\lambda = 416.7$) which approximately coincides with our band α ($\lambda = 415.5$). A second broader band, which is ascribed to samarium, lies at $\lambda = 477.7$, and would thus be also not very far removed from the band δ of the diamond ($\lambda = 471$). However, on the other hand, it must be pointed out that samarium, as well as the second band at $\lambda = 477.7$, also shows a third

equally strong band at $\lambda = 463.2$, no trace of which is to be seen in the diamond, and that, moreover, no single one of the rare earths here considered shows so general an absorption of the ultra-violet as the diamond substance in question appears to possess. Moreover, such an agreement between the position of the absorption bands is further opposed by the difficulty that they are displaced towards one another by a solvent, and, generally speaking, all the more the more the indices of refraction of the solvents differ. According to Kundt's rule it would be expected that the diamond impurities in question in aqueous solution—if they should then show absorption bands, which is not certain—would show the band α further displaced towards the ultra-violet, while the above mentioned samarium band, on the contrary, lies somewhat towards the red.

I endeavoured in another way to obtain a hint by the determination of the specific gravity, but the differences between the stones with the faint and those with the strongly marked band α were so small and so fluctuating that nothing could be deduced from them. Schrotter (*Wien. Ber.*, 1871, lxi., p. 467) found, for example, for three larger pale yellow stones the mean specific gravity 3.51465, and for three colourless crystals almost as large, 3.51458, while two other colourless stones gave 3.51869 and 3.51058 respectively.

Also the indices of refraction of the different crystals show no difference which could not be ascribed to errors of observation. But as in this region hitherto only very incomplete, and mostly also very untrustworthy information is obtainable, I give here in conclusion the mean value of several series of examinations performed by me with different crystals, the numbers being correct for 16.

Indices of Refraction of the Diamond.

A	2.40245	E	2.42694
B	2.40735	F	2.43539
C	2.41000	G	2.45141
D	2.41734	H	2.46476

The letters denote Fraunhofer's lines.—*Annalen der Physik und Chemie*, xli., 1891, 505.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING APRIL 29TH, 1905.

By SIR WILLIAM CROOKES, F.R.S.,
and
SIR JAMES DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, May 10th, 1905.

SIR,—We submit herewith, at the request of the Metropolitan Water Board, the results of our analyses of the 209 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the Metropolitan Water Board taking their supplies from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 29th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 209 samples examined by us during the month, all were clear, bright, and well filtered.

The rainfall at Oxford during April was fairly evenly spread over the month, rain having fallen on twenty days. The amount measured was 1.94 inches, and as the average for April is 1.61 inches, we have an excess of 0.33 inch. Deducting this excess from the previous deficit of 1.22 inches, we still have a deficit of 0.89 inch, or 12.8 per cent, on the thirty-five years' average.

Our bacteriological examinations of 359 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 714 others from special wells, standpipes, &c., making 1073 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 23 samples) ..	106
New River, filtered (mean of 64 samples) ..	13
Thames, unfiltered (mean of 22 samples) ..	4887
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 182 samples) ..	19
Ditto ditto highest	229
Ditto ditto lowest	0
River Lea, unfiltered (mean of 23 samples) ..	175
River Lea, from the East London District clear-water wells (mean of 22 samples) ..	27
Kent District, from the wells at Deptford (mean of 23 samples) ..	3

Of the 291 daily samples taken from the general wells of the Metropolitan Water Board, eighteen samples, or 6.1 per cent, were sterile. Thirteen samples, or 4.4 per cent, contained more than 100 microbes per c.c., and of these five samples contained more than 150 microbes per c.c. The thirteen excess samples contain an average of 142 microbes. In March there was only one excess sample which contained more than 150 microbes per c.c.

While the general condition of the London supply is excellent, there has been during the past month a slight increase in the organic matter (chiefly vegetable) in solution, with a corresponding slight access of colour, due to the greater rainfall. The microbic condition is very satisfactory, due to the combined efficiency of the storage and filtration.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

TWELFTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1904.*

By F. W. CLARKE.

(Concluded from p. 228).

Tungsten.

THE determinations by Smith and Exner of the atomic weight of tungsten represent the culmination of ten years' work in the laboratory of the University of Pennsylvania (*Proc. Am. Phil. Soc.*, xliii., 123; a condensation of the memoir was given in the *Journ. Am. Chem. Soc.*, xxvi., 1082). Many methods of determination were examined, with many failures, and unforeseen difficulties in the purification of material had to be overcome. Finally, pure compounds of tungsten were obtained, and with them the new measurements were made.

First, tungsten hexachloride was converted into trioxide by decomposition with water and ignition of the residue at a dull red heat. All weights were reduced to a vacuum, and the antecedent atomic weights were O = 16 and Cl = 35.45. Twenty-seven determinations were made, as follows:—

Weight WCl ₆ .	Weight WO ₃ .	Atomic weight W.
3.18167	1.86085	184.04
2.66612	1.55903	183.94
3.52632	2.06244	184.05
1.52117	0.88972	184.07
1.22299	0.71523	184.00
2.28445	1.33903	184.01
3.25404	1.90337	184.10
3.37078	1.97133	184.01
7.76488	4.54082	183.98
2.08764	1.22114	184.11
2.80141	1.63859	184.09
3.24328	1.89681	184.02
4.97975	2.91262	184.06
3.04036	1.77838	184.10
4.31046	2.52133	184.10
2.21201	1.29381	184.07
2.70368	1.58135	184.06
3.60658	2.10934	184.03
2.63037	1.53835	184.02
3.41668	1.99808	185.07
3.49940	2.04675	184.06
3.86668	2.26145	184.05
3.40202	1.98970	184.03
3.20661	1.87533	184.01
3.26386	1.90909	184.09
6.73833	3.94031	183.94
7.37889	4.31643	184.14
Mean		184.04

Secondly, twenty-three determinations were based upon the conversion of metallic tungsten into trioxide, with the subjoined results:—

Weight W.	Weight WO ₃ .	Atomic weight W.
2.24552	2.83144	183.96
1.78151	2.24619	184.07
1.63590	2.06270	183.98
1.38534	1.74665	184.04
1.29903	1.63774	184.09
2.01302	2.53781	184.12
2.18607	2.75632	184.01
2.36755	2.98478	184.12
1.94958	2.45781	184.12
4.43502	5.59141	184.09
2.37603	2.99548	184.11
2.58780	3.26260	184.08
2.58503	3.25886	184.14
2.38298	3.00441	184.06
2.05578	2.59169	184.13
3.60828	4.54915	184.08
6.22621	7.84949	184.11
5.28444	6.66239	184.08
3.99095	5.03138	184.12
7.30166	9.20647	184.00
3.44143	4.33870	184.10
2.67709	3.37541	184.01
4.96735	6.26229	184.13
Mean		184.07

The mean value 184.05 probably approximates very closely to the atomic weight of tungsten.

Neodymium and Praseodymium.

Auer von Welsbach's recent atomic weight determinations for these two metals are given without weights or details as to the method employed (*Sitzungsber. Akad. Wiss. Wien.*, cxii., 1037). His figures, referred to O = 16, are as follows:—

Pr.		Nd.
140°64		144°55
140°50		144°52
140°56		144°57
140°57	Mean..	144°54

Samarium.

Urban and Lacombe have deduced the atomic weight of samarium from analyses of the sulphate $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ (*Comptes Rendus*, cxxviii., 1166). The material studied was derived partly from gadolinite, partly from earths obtained from monazite sand, and the absence of europium and gadolinium was rigorously proved. The data are subjoined.

Weights.			Atomic weight.		
A. $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$.	B. $\text{Sm}_2(\text{SO}_4)_3$.	C. Sm_2O_3 .	From A : B.	From B : C.	From A : C.
1.0499	0.8435	0.4996	150.24	150.33	150.31
1.2898	1.0362	0.6137	150.19	150.30	150.28
1.3650	1.0969	0.6497	150.58	150.34	150.39
1.7992	1.4453	0.8557	150.04	150.16	150.13
1.8636	1.4977	0.8873	150.71	150.44	150.50
0.8407	0.6749	0.4001	149.08	150.72	150.35
2.5107	2.0172	1.1948	150.30	150.34	150.33
3.1171	2.5045	1.4840	150.36	150.50	150.47
2.9425	2.3635	1.4001	149.91	150.49	150.36

Means . . . 150.157 150.402 150.347

Two additional analyses gave the following figures :—

2.2200	2.5874	1.5324	150.37	150.33	150.34
2.8382	2.2804	1.3508	150.35	150.37	150.37

The value finally adopted for the atomic weight of samarium is 150.34, when $O = 16$. The value taken for sulphur is not stated, nor is anything said concerning a reduction of the weights to a vacuum.

A single determination of this atomic weight by Kappel is given by Muthmann and Weiss (*Liebig's Ann. Chem.*, cccxxxi., 16). 1.1267 grms. $\text{Sm}_2(\text{SO}_4)_3$ gave 2.45028 grms. Sm_2O_3 ; hence $\text{Sm} = 151.39$. This figure is a unit higher than that found by Urban and Lacombe.

Europium.

The atomic weight of europium has been determined by Urban and Lacombe, who analysed the octohydrated sulphate (*Comptes Rendus*, cxxviii., 627). Their calculations are based on $O = 16$, although it is not stated what value was assumed for S. Neither are we informed whether the weights were reduced to a vacuum. The data are as follows :—

Weights.			Atomic weight.		
A. $\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$.	B. $\text{Eu}_2(\text{SO}_4)_3$.	C. Eu_2O_3 .	From A : B.	From B : C.	From A : C.
1.7787	1.4303	0.8500	151.58	151.77	151.72
2.4785	1.9935	1.1848	151.94	151.80	151.83
2.4777	1.9449	1.1554	152.17	151.61	151.74
2.4831	1.9968	1.1870	151.639	151.89	151.83
2.2988	1.8488	1.0990	151.80	151.88	151.86

Means . . . 151.826 151.790 151.796

The second of these means, representing the ratio $\text{Eu}_2(\text{SO}_4)_3 : \text{Eu}_2\text{O}_3$, is assumed to be most nearly correct.

Gadolinium.

Two determinations of the atomic weight of gadolinium are given by Marc (*Zeit. Anorg. Chem.*, xxxviii., 128). The usual method of synthesis of sulphate from oxide was employed. The figures given are—

Weight Gd_2O_3 .	Weight $\text{Gd}_2(\text{SO}_4)_3$.	Atomic weight
0.2201	0.3666	156.30
0.2444	0.4070	156.35

These results agree closely with those reported by Bettendorff and Benedicks.

Thorium, Carolinium, Berzelium.

Baskerville has continued his investigations upon the complexity of ordinary thorium, and has separated the fractions by preparing and distilling the chlorides in quartz tubes (*Journ. Am. Chem. Soc.*, xxvi., 922). The non-volatile residue gave an oxide soluble in concentrated hydrochloric acid, from which the chloride so produced was re-crystallised several times. From this chloride the oxide was prepared, and atomic weight determinations were made by the sulphate method. The metal of the oxide was assumed to be a tetrad, and upon that basis the following results were obtained :—

Weight oxide.	Weight sulphate.	Atomic weight metal.
1.559290	2.434914	255.5
0.524254	0.819365	255.9
0.549331	0.854810	255.6

To this element the name carolinium is given.

The volatile chloride obtained in the first part of the distillation, converted into oxide, gave the subjoined values :—

Weight oxide.	Weight sulphate.	Atomic weight metal.
0.306778	0.505705	213.5
0.320618	0.530890	212.0
0.794692	1.3309245	212.7

This series represents the element which Baskerville has named berzelium.

Finally, the thorium, which had been freed in great measure from carolinium and berzelium, was also examined.

Weight oxide.	Weight sulphate.	Atomic weight Th.
0.425456	0.694934	220.6
0.740052	1.210405	220.1

These data are only preliminary, but they strongly support the fundamental conception upon which the research was based.

Miscellaneous Notes.

Guthe has re-measured the electro-chemical equivalent of silver, and finds it to be 1.11683 m.grms. per coulomb (*Bull. Bureau of Standards*, i., 21). A similar determination by Van Dijk and Kunst gave 1.11818 (*K. Acad. Wetén, Amsterdam, Proc. Section of Sciences*, vi., 441). The unavailability of an electrolytic comparison with silver for determining the atomic weight of antimony was mentioned in the Report for 1903. The investigation there referred to has been continued by Cohen, Collins, and Strengers, and the former results are confirmed (*Zeit. Phys. Chem.*, i., 291). The apparent atomic weight of antimony increases with the concentration of the solution from which it is deposited. Methods for determining the atomic weights of the rare earths are discussed by W. Wild, who compares the volumetric and gravimetric processes (*Zeit. Anorg. Chem.*, xxxviii., 191). Rudolf has investigated the atomic weight of radium as deduced from regularities between the spectral lines, and favours the preliminary acceptance of $\text{Ra} = 225$ (*Zeit. Phys. Chem.*, i., 100). There are also memoirs on the general subject of the spectral regularities by Runge (*Zeit. Elektrochem.*, x., 119) and by Watts (*Phil. Mag.*, Ser. 8, p. 279). Wetherell has studied the relations between the atomic weights, and sought to explain their anomalies (*CHEMICAL NEWS*, xc., 260, 271). On the vexed question of the standards there is another defence of the hydrogen unit by Erdmann (*Chem. Zeitung*, xxviii., 679), and the same chemist has proposed a table of rounded off values for ordinary use (*Zeit. Angew. Chem.*, xxxviii., 1397). The International Table for 1905 appeared in the *CHEMICAL NEWS* for January 27, 1905 (vol. xci., p. 44).

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY.

CONVERSAZIONE AT BURLINGTON HOUSE.

ON Wednesday, the 17th inst., a *Conversazione* was held at the Royal Society's Rooms, Burlington House. It was well attended, and the exhibits were of considerable interest. Among those which attracted most attention we may mention the following:—

Specimens illustrating the Action of Light and of Radium upon Glass, exhibited by Sir WILLIAM CROOKES, F.R.S.

1. It is well known that many samples of colourless glass containing manganese slowly assume a violet tint when exposed to sunlight. This effect is frequently seen in plate-glass windows having a southern aspect; watched from year to year they assume a more and more pronounced amethystine hue. The introduction of manganese into glass is to neutralise the colour caused by the presence of iron. Iron gives the glass a greenish tint, and the addition of manganese binoxide performs the double function of oxidising the green proto-salt of iron to the per-salt, and also of imparting a purple shade which neutralises the green-yellow tint of the silicate of peroxide of iron. In 1903, I received from two separate correspondents specimens of glass coloured an intense purple. The pieces of glass are of all depths of tint, from deep violet, almost black in thick pieces, to pale amethyst. Analysis shows the glass to contain manganese. Heating the glass in a covered crucible to its softening point discharges the colour, leaving the glass white and transparent. The coloration is not superficial. On immersing a piece of the coloured glass in a liquid of about the same refractive index as itself, the colour is seen to have penetrated throughout the mass. Radium, acting for a few days, even through quartz, will produce as intense a coloration in a piece of this glass as exposure to the sun on the Pampa has taken years to effect. A piece of the coloured glass, bleached by heat, was put close to a quartz tube in which about 15 m.grms. of pure radium bromide was sealed up. In the course of a few hours a faint amethystine tint could be distinguished on the glass, and in a week the tint was equal to the deep colour of the unbleached specimen. A duplicate piece of the same glass which had been bleached by heat, kept away from radium, remained colourless for seven weeks.

2. (Lent by Prof. J. W. Judd, C.B., F.R.S.). Six pieces of glass from the greenhouses at Kew Gardens. No. 1 shows the colour (due to iron oxide) which was originally adopted for the greenhouses in accordance with the recommendations of the late Mr. Robert Hunt, F.R.S. Nos. 2, 3, 4, illustrate the fading due to the action of sunlight. No. 5 has become perfectly colourless, while in No. 6 the purple tint, due to a small admixture of manganese oxide in the frit, has been developed. This series of changes has taken probably about fifty years to complete in our climate. The purple spots in Nos. 1 and 6 were produced by Sir William Crookes by the action of 15 m.grms. of radium bromide in a quartz tube in the course of ten days, the beginning of change being well marked at the end of two days.

3. (Lent by Prof. H. McLeod, F.R.S.). Manganese glass exposed to light for forty years. A portion of a pane of glass from a greenhouse belonging to Turner, of Slough. The greenhouse had formerly been erected at Reading. It will be observed that the ends of the glass which had been protected from light by the window frame remain colourless. The specimen was given to the exhibitor in 1886 by the late Mr. H. G. Madan, of Eton College. In the expectation that radium might have a reducing effect on the manganese compound, Mr. F. Soddy submitted a portion of the pane to the action of 30 m.grms. of radium bromide for three days in May, 1904. The colour, however, instead of being diminished was intensified.

4. (Lent by Mr. G. T. Beilby). Specimens illustrating the coloration of glass, quartz, and fluor-spar by the β -rays of radium.

Mr. G. T. BEILBY showed the Phosphorescence caused by the β -rays of Radium. Phosphorescence of calc spar and other substances:—(1) During exposure to the rays; (2) after removal from the rays; and (3) revived by heat after secondary phosphorescence has died down. The storage of phosphorescence and the coloration effects are due to partial electrolysis of the calcium carbonate or other substances, by the stream of negative electrons. A proportion of the ions re-combine at once, others continue to re-combine after the rays have ceased to act, and the remainder only re-combine when the mobility of the crystal molecules is increased by heat.

Prof. J. A. FLEMING, D.Sc., F.R.S., exhibited:—

1. A direct reading Cymometer for measuring the length of the Waves used in Wireless Telegraphy. The instrument consists of a sliding tubular condenser and an inductance coil, the capacity and inductance being varied together in the same proportion by one movement of a handle. The circuit is closed by a copper bar which is placed alongside of the aerial wire indicating the electric waves. The handle of the cymometer is then moved until a Neon vacuum tube used as an indicator shines most brightly and thus determines when the cymometer circuit is tuned to the frequency of the aerial. A pointer moving over a scale then indicates the wave length of the radiated wave in feet or metres.

2. An Oscillation Valve for rectifying Electrical oscillations and rendering them measurable on an ordinary Galvanometer. The valve consists of a bulb enclosing a carbon filament made like an incandescence lamp. The filament is surrounded by a metal cylinder. The bulb is highly exhausted. When the filament is incandescent, negative electricity can move through the vacuum from the hot filament to the cylinder, but not in the reverse direction. Hence the arrangement can separate out the two opposite currents in an electric oscillation. It can be used in combination with a dead beat galvanometer as a receiver in wireless telegraphy. The valve replaces the coherer and other appliances, and the signals are given by long and short deflections of the galvanometer.

Mr. CARL ZEISS showed an Optical Appliance to facilitate visual perception of Ultra Microscopic Particles. The apparatus consists of a projection table provided with an arc lamp, optical bench, two projection aplanats, and a precision slit. (The use of sunlight instead of the arc lamp is preferable). The image of the source of light is projected on to the precision slit by means of one of the aplanats, the second aplanat then serves for the purpose of projecting an image of the slit, reduced to $1\frac{1}{2}$ diameters, at a distance of about 90 m.m. from the lens. The microscope situated at the end of the optical bench, and fitted, for the observation of fluids, with a water immersion objective D* and a special trough with quartz windows, is used upright, and the objects illuminated horizontally with a very narrow beam of light. An achromatic objective, mounted on a sole plate with cross slide, serves as a condenser. Either fluids or solid objects may be observed. Particles of far less than half a wave length can be made visible.

In the Principal Library Sir WILLIAM CROOKES, F.R.S., exhibited photographs of the "Cullinan" Diamond which he had recently taken.

MESSRS. ISENTHAL and Co. exhibited:—

1. Resonance Induction Coil and High Potential Apparatus. Electrolytic condensers of very large capacity are charged from the mains through the primary of a suitably wound induction coil, and the circuit broken and reversed at zero potential by means of a motor-driven commutator of special construction. The advantages are:—No motor transformer required in primary circuit, no rectifying device in secondary circuit, no interruptors to be

cleaned. Continuous current converted sparklessly into pure sine current suitable for space telegraphy.

2. Resonance Electro Magnet. An electro magnet excited from the source described above exhibits peculiar physical and physiological phenomena.

The Director of the National Physical Laboratory exhibited High temperature Electric Furnaces. These furnaces are constructed of rare earths such as are used in Nernst lamps. They are available for temperatures between 800° and 2000° C. The apparatus used in a recent determination of the melting-point of platinum is shown at work, in addition to that for other experiments of a similar character.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., showed the Action of Actinium or Emanium emanation on a Sensitive Screen. Actinium or emanium are different names, adopted by Debiere and Giesel, respectively, for the same substance, separable from pitchblende, and accompanying lanthanum. It gives off an emanation, whose period of activity is very short—a few seconds. When this emanation impinges on a sensitive zinc sulphide screen, the screen becomes luminous. The luminous patch can be blown away, and in a second or two reappears.

Mr. H. J. BROOKS exhibited an Oil Painting. A Friday Evening Lecture at the Royal Institution of Great Britain.

Messrs. R. and J. BECK, Ltd., exhibited:—

1. Microscope and Goniometer stage. Designed by Dr. Evans, and made for the Imperial Institute for examining the optical qualities of minute grains of sand.

2. Set of Petrological Quartz Wedges. 1. Quartz wedge on slip giving 7 orders. 2. Quartz wedge on slip giving 22 orders. 3. Dr. Evans's double quartz with two wedges (placed side by side), which are cut at an angle of 90° from the same plate, showing 7 orders.

3. Photo-micrographic Camera. Designed by Mr. J. W. Gordon for taking small direct photo-micrographs while the instrument is in use after observation without attention to the adjustments. It consists of a short tube carrying a projecting lens and a photographic plate which is placed over the eye-piece of the microscope focussed in the ordinary manner, and exposed by means of a shutter in front of the projecting lens. A complete daylight developing and filling apparatus is supplied, so that a number of photographs can be taken without recourse to a dark room and without any other appliances.

Prof. A. SCHUSTER, F.R.S., exhibited a Large Echelon Spectroscope. This echelon spectroscope, constructed by Messrs. Adam Hilger, Ltd., consists of 33 plates, and has a resolving power equal to that of an ordinary grating of 329,000 lines in the first order.

Prof. ERNEST FOX NICHOLS exhibited:—

1. Torsion Balance, used in Radiation Pressure Measurements, by Nichols and Hull.

2. Vacuum Tube, of Nichols and Hull (in action), to illustrate the Repulsion of Comet Tails by the Sun. (See *Astrophysical Journal*, vol. xvii., 1903).

Mr. R. S. HUTTON exhibited New models of Laboratory Electric Furnaces. The furnaces consist of a carbon tube, rod, or plate heated by an electric current. In the tube furnaces the carbon is surrounded by some material of low thermal conductivity which also serves to protect the hot tube from oxidation. The substance to be heated is placed in a carbon boat or crucible inside the tube, and can thus be brought to a very high temperature. The method employed for conveying the current to the carbon by soldering water-jacketed sleeves to the electro-coppered ends of the carbon forms a novel feature of the construction. The rod and plate types of furnace are used for melting or heating up material placed around the carbon. Some samples of refractory oxides, fused in the electric furnace, are included in the exhibit.

Mr. R. A. HADFIELD, M.Inst.C.E., exhibited a Series of Alloys of Iron and Steel tested at Liquid Air Tem-

perature. The specimens exhibited are selected from about 300 bars used and tested for the research at the Royal Institution by Sir James Dewar. They show the effect of liquid air (temperature -182° C.) upon almost pure iron (Swedish charcoal iron "S.C.I.," 0.04 carbon, 99.82 iron), and a large number of alloys of iron with other elements. The well known ductility of iron is shown to disappear, and its tenacity is more than doubled. Similar effects occur with nearly all the alloys of iron with carbon and other elements, except those containing nickel, which metal appears to considerably modify the embrittling effect of low temperatures upon iron. Iron alloyed with nickel in combination with manganese (No. 1414B, 1 per cent carbon, 6 per cent manganese, 24 per cent nickel) becomes not only more ductile, elongating 57 per cent at -182° C. against 42 per cent at atmospheric temperature. Its ultimate tenacity is also increased from 49 to 75 tons per square inch.

Sir OLIVER LODGE, F.R.S., gave a demonstration of the use of Electric Valves for the production of High Tension Continuous Current. Electric vacuum valves, which it is now found were suggested in a letter by Sir George Stokes twenty years ago, have as their function the *entrapping* of a portion of electricity by permitting its passage in one direction, and stopping its return. They therefore can be employed to accumulate electricity supplied from an intermittent or jerky source, and to store it at a steady high potential; so that it may thereafter maintain a current through a very high resistance, as in electrostatics, and may produce X-rays, or point-discharge, or other continuous high tension effects; and may enable a small portable coil to imitate some of the effects of a much larger one by storage and accumulation of impulses. Among the applications contemplated are the separation of metallic fume and the dissipation of fog.

PHYSICAL SOCIETY.

Ordinary Meeting, May 12th, 1905.

Dr. C. CHREE, F.R.S., Vice-President, in the Chair.

Dr. A. D. DENNING described a simple method of determining the Radiation Constant, suitable for a laboratory experiment.

The apparatus consists of a hemispherical copper cap to the outside of which is affixed a jacket through which steam or water can be passed. The receiving surface consists of a silver plate, and the rate of rise of temperature of the plate is measured by means of a silver-constantan thermo-junction. When performing the experiment, a non-conducting pad is placed between the hemisphere and the silver disc till the temperature of the jacket is uniform. Then the pad is slid out, and the deflections of the galvanometer in the thermo-junction circuit are noted every few seconds. By plotting these deflections on a curve the initial slope of the curve, *i.e.*, the initial rate of rise of temperature of the silver disc, is obtained; and from this, knowing the constants of the disc, &c., the radiation constant can be calculated. The author gives some numbers which indicate that a very fair degree of accuracy can be obtained.

Prof. CALLENDAR asked what steps had been taken to protect the area of the edges of the silver disc, which appeared to be about half the area of the upper surface, from the oblique radiation of the hemisphere. The upper surface alone was taken as the effective area in the calculation. He had found this difficulty in applying the Crova disc method to the measurement of radiation in a previous case, although the radiation was nearly parallel and normal to the disc, instead of being distributed over a hemisphere. He thought that greater sensitiveness would be obtained by using a single short constantan wire for the couple. It was necessary that this wire should be

exceedingly fine to prevent error in the temperature-measurement owing to cooling of the end near the junction by conduction. A copper disc appeared preferable to a silver disc as reducing the number of junctions of different metals. The constantan wires used by the author did not appear to be fine enough to eliminate this source of error, which, however, would tend to compensate the error introduced by the neglect of the area of the exposed edges of the disc.

Mr. CAMPBELL asked whether the convection-currents do not introduce considerable error. The effect of the rim of the disc could be made of relatively less importance by increasing the diameter of the disc.

The AUTHOR, in reply, said that of course the effect of the edge of the disc would be reduced by decreasing the thickness; but it would not do to make the disc too thin, as the conductivity would then be too small. As to convection-currents, he thought that in the method of conducting the experiments employed these were unlikely to be of much importance.

Prof. H. L. CALLENDAR read a paper on "*A Bolometer for the Absolute Measurement of Radiation.*"

It is now generally agreed that the electric compensation method, in which the heat received by radiation on a metallic strip is determined by measuring the electric current required to produce the same rise of temperature in the strip, is the most satisfactory and accurate method for absolute measurement. Two methods have been used for this purpose:—(1) The thermoelectric method of Angström, in which the equality of temperature between the strip exposed to radiation and that heated by the current is determined by means of a copper constantan couple, the two junctions of which are attached to the backs of the two strips with silk paper and shellac; (2) the bolometric method of Kurlbaum, in which the rise of temperature produced by the radiation or by the electric current is measured by the increase of resistance of the metallic strip itself. In applying the first method it is necessary to use a sensitive galvanometer for the thermocouple, and an accurate milliammeter for the current. It is also necessary to make measurements with the strips interchanged, as it is impossible to secure exact equality of resistance of the strips, and exact equality of thermal contact for the junctions which are insulated from the strips by paper and shellac. The advantages of the second method, which has not hitherto been applied to the extent which it merits, are:—1. That the strip is also the thermometer, and can therefore be made much thinner and quicker in action as no paper insulation is required. 2. That the power available is much greater, so that the same portable milliammeter which serves for measuring the current may also be used for the resistance-balance in place of a sensitive galvanometer. 3. That the actual resistance of the strip may readily be verified at the time without special additional apparatus. 4. That uniformity of resistance of the strip is less important than in the thermoelectric method, in which the mean resistance of the strip is not necessarily the same as the resistance at the central point where the temperature is taken by the couples. 5. That the area exposed to radiation may be more accurately measured.

In the practical application of the bolometric method for the absolute measurements of solar radiation, the author has introduced certain modifications suggested by experience in platinum thermometry, with the object of securing:—(1) Temperature compensation, so that the zero remains constant in spite of changes in the surrounding temperature; (2) conduction compensation, so that loss of heat by conduction at the ends of the strips may not affect the readings; (3) Accurate measurement of the area of radiation absorbed. 1. In order to secure accurate temperature compensation during the observations of radiation, when changes of temperature of the instrument are sometimes unavoidable, especially with powerful sources of radiation, in spite of the water-jacket in which the instrument is enclosed, the bolometer is

balanced against a balancing resistance constructed of the same platinum, enclosed in the water-jacket, but protected from the radiation. 2. To secure conduction compensation, this balancing resistance is made in two parts, one (a) precisely similar to the bolometer itself, but with strips 1 c.m. long instead of 3 c.m., so that the ends of the strips are subject to the same conduction losses as those of the bolometer when heated by the electric current, the change of resistance measured being that of the central 2 c.m. only of the strips, which length is uniformly heated. The other part (b) of the balancing resistance is replaced by a resistance of manganin when the actual temperature of the bolometer or the heating effect of the current is measured. 3. To secure accurate measurement of the area of radiation absorbed, this area is determined by an aperture in the cover of the water-jacket having a width of 2 c.m. coinciding with the central portions of the bolometer-strips. The strips are arranged with a small overlap, so that all the radiation entering this area falls on the strips. The necessity of accurate measurement of either the length or the width of the strips themselves is thereby avoided. With these modifications the bolometric method appears equal in convenience, and probably superior in accuracy to the thermoelectric. Owing also to the great increase in power available, the absolute measuring bolometer can be directly used with one of the author's self-recording instruments for solar radiation.

Comparisons have been made between the bolometer, in which the platinum strips are directly exposed to radiation, and one of the author's ordinary sunshine receivers enclosed in a glass bulb, in order to determine the effect, if any, of the glass bulb in selective absorption. The values of the reduction constant obtained for the glass receiver showed no certain variation over a wide range of quality of radiation, from sunshine or arc-light down to a dull red heat. This result is probably to be attributed to a self-compensating action of the glass bulb, which radiates to the enclosed coils precisely those rays which it absorbs.

Mr. CAMPBELL pointed out that with regard to the comparison made by Professor Callendar between the open and the glass-covered bolometers, it should be noticed that the radiation used in the experiment had already passed through the glass of the globe surrounding the glowing filament. This would filter out some part of the radiation, possibly in such a way as to make the two instruments agree more closely than they otherwise would.

Mr. PRETTY suggested that bolometers such as the author describes might be used for testing the Watts given out by incandescent lamps.

Prof. AYRTON wished to draw special attention to the effect to which Mr. Campbell had alluded, namely, the fact that the radiation used by the author had already been filtered by passing through glass before it reached the glass-enclosed bolometer.

Dr. CHREE inquired whether the Angström instrument was effected by lag, and to what extent.

Prof. CALLENDAR said that in his experience the Angström instrument took nearly one minute to reach within 1 per cent of its steady reading. He had made comparisons with the naked arc as well as with the enclosed incandescent source, and found the results did not differ materially. The glass-enclosed receiver also gave consistent values of the reduction constant when compared with the Angström instrument or the bolometer, which were not screened by glass.

Mr. W. H. PRICE read a paper on the results of experiments carried out at Crompton's Works at Chelmsford, by Mr. C. H. Wright, on the possibility of using the resistance of a conductor heated by an alternating electric current as a measure of the current.

An alternating current was passed through a thin conductor in series with a standard resistance, and a small direct current from a storage-battery superposed on the system. The mean differences of potential at the terminals enabled him to compare the resistances on a potentiometer.

meter. The presence of any considerable body of air near the heated conductor was found to affect the results through the irregular currents of air produced, while the neighbourhood of solid matter caused the permanent condition to be reached only slowly in consequence of its heat capacity. To obtain uniform results so that the resistance of the conductor corresponded consistently and promptly to the current passing, it was found necessary to enclose the conductor in a relatively large vessel exhausted of air. Nearly consistent results were then obtained, affected, however, to some extent by the changes in the vacuum by the liberation of gas occluded in the conductor. At moderately good degrees of exhaustion the resistance of the conductor for a given current varies rapidly with the quantity of gas that remains, and it was suggested that this might form the basis of a vacuum gauge.

The results of experiments on carbon incandescent lamps, and on platinum-foil ligaments in exhausted bulbs, were shown in diagrams, giving the effects of different air temperatures, and of the degrees of exhaustion. The author supposed that such conductors enclosed in large glass bulbs, highly exhausted when the conductors are incandescent, would form useful gauges for electric currents. They would be perfectly portable, not easily liable to damage, capable of highly accurate and permanent calibration, and of course very inexpensive. They could be made of exceedingly small inductance and capacity, and their values would be independent of periodicity and wave-form. Their employment would correspond in precision and sensitiveness to other measurements of electrical resistance. The useful range of currents measured by one such conductor might be of the order of 1 to 4.

Prof. AYRTON pointed out that, at any rate for small alternating currents, a suitably wound instrument of the Kelvin-balance type was quite sufficiently accurate.

Mr. CAMPBELL asked was any compensation introduced for the temperature of the walls of the enclosure, or was the temperature merely read and a correction made for it?

The AUTHOR, in his reply, said that in all cases corrections were applied for the external temperature.

NOTICES OF BOOKS.

Annual Reports on the Progress of Chemistry for 1904.

Issued by the Chemical Society. London: Gurney and Jackson. 1905.

This book is the result of a new departure on the part of the Chemical Society, the Council having decided to issue annually a report of the progress of the science, and there can be no doubt that these reports will be given a very hearty welcome by all classes of chemists. The articles necessarily amount to very little more than brief notes, but they will be of considerable value even if regarded only as calling attention to special points in which essential advances have been made during the year, and giving references to original papers for further reading on matters of importance. The subject has been divided under the same headings as have been adopted for the classification of the Society's abstracts, and the authors of the articles may in all cases be regarded as authorities in the special province of which they treat. Organic chemistry is accorded the largest amount of space, and is sub-divided into two separate articles. A very interesting paper by Mr. Soddy on "Radio-activity" differs from the other articles in going back to the original discovery of radio-activity in 1896, and thus giving more than a general *résumé* of the year's work, and it is hardly necessary to say that it gives an excellent summary of the present state of our knowledge of the subject. These annual reports will be among the most useful of the Chemical Society's publications, and will be found almost indispensable by teachers and others.

Optical Pyrometry. By C. W. WADSWORTH and G. K. BURGESS. Washington: Government Printing Office. 1905.

THIS reprint from *Bulletin*, No. 2, Bureau of Standards, describes the experimental examination of the most important types of optical pyrometers carried out by two able investigators in response to constant inquiries addressed to the Bureau respecting the use of pyrometers generally. The authors undertook this research primarily from the point of view of the application of these instruments in industrial processes, and the conclusions they draw will be specially valuable to technical chemists and works' managers. The theory of radiation is lucidly discussed, and the special advantages of the various instruments are fairly and fully described, the section on their comparative merits forming the most useful in the book; the various types are compared from all points of view, and an excellent summary is given of the suitability of the different pyrometers for use under special conditions and for various purposes. A short section on special problems in optical pyrometry concludes a thoroughly practical and useful monograph.

Éléments de Chimie Inorganique. ("The Elements of Inorganic Chemistry"). Part II. By Prof. W. OSTWALD. Translated by L. LAZARD. Paris: Gauthier-Villars. 1905.

THE great and valuable influence which Prof. Ostwald's works have exercised upon the teaching of chemistry makes it most desirable that they should be easily accessible to the students of all nations, and it seems probable that they will ultimately be almost unique as regards the number of translations of them which have appeared. The French version has been prepared from the first edition of the original, but most of the important corrections appearing in the second edition have been introduced into it, and the author has read through the proofs. It only remains to be said that the translation has obviously been very carefully performed, and the meaning of the original is reproduced with exceptional accuracy.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft,
Vol. xxxviii., No. 4, 1905.

Hexahydroxylamine Cobaltic Salts.—A. Werner and E. Berl.—Most ammonia or amino-cobaltic salts—*e.g.*, dichlorodithylenediamine-cobalt chloride in alkaline solution—give, in presence of hydroxylamine, products which, when acidulated with concentrated hydrochloric acid, yield hexahydroxylamine cobaltic chloride, and from this other similar derivatives can be prepared. These salts are all analogous to the hexamino-cobalt salts (luteo-salts); they are all yellow, and somewhat darker in colour than the corresponding ammonia compounds. When perfectly pure they can be kept for some time, but are very readily decomposed when impure, especially if alcohol or ether is present. The chloride has been known to decompose for no apparent reason, giving the cobaltous salt. The formula of the compounds is $[\text{Co}(\text{NH}_2\text{OH})_6]_3\text{X}_3$. The hydroxylamine molecule on entering the complex radical loses most of its usual activity as a reagent, though it still reacts with aldehydes, &c.; well-defined compounds could not, however, be prepared. Thus, four different series of hexamino-cobaltic salts are now known, *viz.*, $\text{Co}(\text{NH}_3)_6\text{X}_3$, $[\text{Co}(\text{NH}_2\text{CH}_2)_3]_3\text{X}_3$, $[(\text{H}_2\text{N})_2\text{Co}(\text{NH}_2\text{CH}_2)_2]_3\text{X}_3$, and

$[\text{Co}(\text{NH}_2\text{OH})_6]\text{X}_3$. These salts resemble one another strongly in both physical and chemical properties; they are all yellow. In their aqueous solutions the properties of the cobalt and of the nitrogenous residue attached to it are completely masked, but they are all strongly trivalent bases.

Applications of Metallic Calcium.—Ernst Beckmann.

—To obtain metallic calcium in a convenient form for use in the laboratory, it may be converted into fine shavings by means of a lathe. As a reducing agent in alkaline solution it reduces nitrobenzene very readily to azoxybenzene, and in hydrochloric acid alcoholic solution the reduction may be continued until aniline is finally produced. Calcium may also be used instead of magnesium for Grignard's reaction. If benzyl iodide dissolved in absolute ether is heated with very finely-divided calcium and a trace of iodine, benzyl calcium iodide, $\text{C}_6\text{H}_5\text{CaI}$, is formed as a light brown powder soluble in ether. If carbon dioxide is introduced into the solution the following reactions take place:— $\text{C}_6\text{H}_5\text{CaI} + \text{CO}_2 \rightarrow \text{C}_6\text{H}_5\text{COOCaI}$, $\text{C}_6\text{H}_5\text{COOCaI} + \text{H}_2\text{O} \rightarrow \text{ICaOH} + \text{C}_6\text{H}_5\text{COOH}$. Ethyl iodide reacts similarly, but far more quickly. The presence of ether is necessary for the reaction, the calcium remaining unchanged in a benzene solution of alkyl halogen. It is possible that a compound of the formula $\text{C}_2\text{H}_5 > \text{O} < \text{R}$ is produced in ether. By means of finely divided calcium metallic oxides and sulphides, e.g., MnO_2 , PbO , CaO , CuS , can be reduced to metals.

Periodic System.—A. Werner.—The author arranges the elements in such a way as to neglect minor analogies and take into account only the general character of each element. This arrangement shows that the whole system consists of a definite number of periods, probably recurring in pairs, each pair including more elements than the last. Of these periods four are known:—(1) A small period, of the elements of which only hydrogen and helium are known; (2) the corresponding lithium and sodium periods, each containing eight elements; (3) the potassium and rubidium periods, each containing eighteen elements; (4) the caesium and radium periods, in the latter of which the only elements known are radium, thorium, and uranium. The following considerations enable us to calculate the number of elements in the incomplete periods. The mean increase in the atomic weight of two consecutive elements can be determined as follows:—

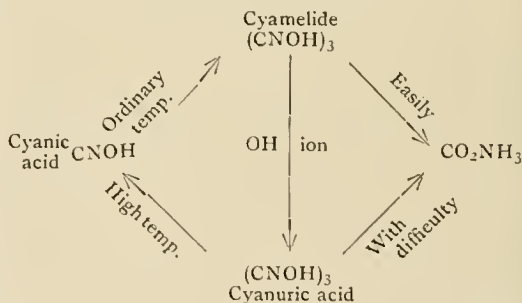
Li period	20·7·03	$\frac{12·97}{7} = 1·85$
Na period	39·9·23·05	$\frac{16·85}{7} = 2·4$
K period	81·12 39·15	$\frac{42}{17} = 2·47$
Rb period	128·85·4	$\frac{42·6}{17} = 2·5$

Thus the mean value of this difference is least in the first period; in the hydrogen-helium period it would be about 1·5, and thus the period would in all probability include three elements—the one still unknown being possibly the prototype of the negative elements. The elements in the lithium and sodium periods are eight in number, i.e., five more than in the first period, while there are eighteen in each of the potassium and rubidium periods, i.e., twice five more than in the preceding periods. In the caesium period the mean difference would be about 2·56.

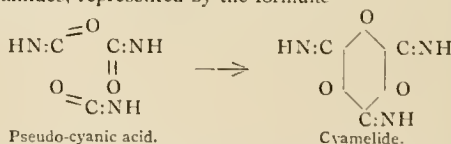
Then $\text{Bi} - \text{Cs} = 208·5 - 133 = 75·5$, $\frac{75·5}{2·56} = 29$. The period should therefore contain 29 elements. Subtracting the number of elements in the preceding period, it appears that fifteen additional elements are to be expected, and these must be the metals of the rare earths. Thus, the following results are obtained:—1 (unknown) and 2 periods—(H, ?, He), each 3 elements; 3 and 4 periods—each 8 ele-

ments = 3+5; 5 and 6 periods—each 18 elements = 3+5 + 2×5; 7 and 8 periods—each 33 elements = 3+5 + 2×5 + 3×5. Investigations of the atomic volume curves show that the elements of the rare earths belong to a period beginning with caesium and ending (at present) with bismuth. It appears that the higher and larger periods are developed from the smaller by the interpolation of intermediate elements which form a transition between the two neighbouring elements, so that they form varieties, as it were, of these elements. In some cases the properties of the elements do not agree with those which should belong to them, taking into consideration their atomic weights and positions in the table; such are A and K, Co and Ni, Te and I, Nd and Pr. It appears on closer investigation that, of these, the third and fourth cases represent as it were the periodic repetition of cases 1 and 2. Thus, argon and potassium occur at the end of Period 2, tellurium and iodine at the end of the fourth period, and six or seven elements from these two are cobalt and nickel and praseodymium and neodymium respectively. As regards the colour of the salts of these elements, the red cobalt salts correspond to the red neodymium salts, and the green nickel salts to the green praseodymium salts; moreover, the colours of the cobalt and nickel salts and those of the neodymium and praseodymium salts are complementary. Thus, even in the deviations from the simple periodicity of properties, the natural system shows certain regularities.

Cyameliide.—A. Hantzsch.—This compound may be prepared by the spontaneous polymerisation of anhydrous cyanic acid, and also from carbonyl chloride and ammonia. A molecular weight determination (carried out in absolute sulphuric acid) shows that it has a fairly low molecular weight, and it may be proved with a fair degree of certainty that it is not a polymer, but an isomer of cyanuric acid. Its formation from cyanic acid is a trimolecular process, $3\text{CNOH} \rightarrow (\text{CNOH})_3$, and hence the lowest formula must be $(\text{CNOH})_3$. Cyameliide is only apparently more chemically indifferent than cyanuric acid, actually it is more readily decomposed, and thus more labile, e.g., even on long-continued boiling with water it is decomposed into CO_2 and NH_3 . The conversion of cyanuric acid into cyameliide is neither possible directly nor in the form of derivatives, but only indirectly by means of the monomolecular HCNO . The relation between the three substances is indicated by the following scheme:—



Theoretical considerations appear to show that cyameliide and (pseudo) cyanuric acid are structurally isomeric tri-carbamides, represented by the formulae—



Preparation of Yellow Arsenic.—Alfred Stock and Werner Siebert.—A solution of yellow arsenic in carbon disulphide may be very easily prepared by letting an electric arc play between arsenic electrodes in carbon di-

sulphide. The anode need not be of arsenic, but may be made of carbon, and the cathode is a piece of an alloy of equal parts of arsenic and antimony. The arsenic is converted into vapour, and condenses in the CS_2 in the form of the yellow modification. It is not advisable to aim at getting very strong solutions (stronger than about 1 per cent), as the yellow variety then appears to be partially converted into the black insoluble form. The solution may be concentrated by distilling off some of the CS_2 .

Halogen Double Salts of Tetravalent Antimony.—R. F. Weinland and Hans Schmid. The authors have prepared $2\text{RbCl} \cdot \text{SbCl}_4$, which forms isomorphous mixtures with rubidium-platinum chloride. These isomorphous mixtures contain varying amounts of platinum, and are of a more or less deep violet colour, according to the amount of antimony in them. Similar isomorphous mixtures of antimony tetrachloride with tin tetrachloride double salts can be prepared, and in them the rubidium can be replaced by ammonium or potassium. In a solution of antimony tri- and pentachloride a state of equilibrium exists between these two compounds and antimony tetrachloride:— $\text{SbCl}_3 + \text{SbCl}_5 \rightleftharpoons 2\text{SbCl}_4$. If a colourless hydrochloric acid solution of antimony trichloride is mixed with the yellowish green solution of the pentachloride in equivalent solutions, according to the concentration of the hydrochloric acid, more or less yellowish brown coloured liquids are obtained, and the liquids are darker the more hydrochloric acid they contain; moreover, the darker they are the more tetravalent antimony they contain. On warming, the colour becomes darker, and thus when hot they contain more tetrachloride. Also, on leading chlorine into a solution of the trichloride in hydrochloric acid, the tetrachloride is formed as an intermediate product, as may be seen by the dark brown colour it assumes before it acquires the light yellowish green tint of the pentachloride. Besides

these salts of formula SbCl_6R_2 , the authors have obtained brown compounds, which appear to be double compounds of the formula SbCl_6R_2 with double salts of SbCl_3 and SbCl_5 , e.g., $\text{SbCl}_6\text{R}_2 \cdot 2\text{SbCl}_6\text{Rb}_3$.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 8th inst., Sir James Crichton-Browne, Treasurer and Vice-President in the Chair. Mr. W. R. Bousfield, K.C., M.P., Mr. A. T. Franklin, Mr. R. Howlett, Mr. D. Nicholson, Professor J. J. Thomson, and Major-General Sir Alfred Edward Turner, K.C.B., were elected Members. The Special Thanks of the Members were returned to Mrs. Frank Lawson for her Donation of £50 and to Sir Thomas H. Sanderson, G.C.B., for his Donation of £55s. to the Fund for the Promotion of Experimental Research at Low Temperatures, and to Mrs. Barton for her Present of a Portrait of Dr. Thomas Young. It was announced that His Grace the President had nominated the following Vice-Presidents for the ensuing year:—Sir William de W. Abney, K.C.B., Mr. Shelford Bidwell, The Right Hon. Lord Alverstone, G.C.M.G., Dr. Ludwig Mond, The Right Hon. The Earl of Rosse, K.P., Sir Thomas H. Sanderson, G.C.B., Sir James Crichton-Browne (Treasurer), and Sir William Crookes (Honorary Secretary). The Right Hon. Lord Rayleigh, O.M., F.R.S., was elected Honorary Professor of Natural Philosophy, and Professor J. J. Thomson, F.R.S., was elected Professor of Natural Philosophy.

Structural Formula of Triphenylmethyl.—A. E. Tschischibabin. If Heintschel's biquinoid formula for triphenylmethyl were correct the hydrocarbon should pass readily into $(\text{C}_6\text{H}_5)_2\text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{C}_6\text{H}_5)_2$, a transformation which has never yet been observed. The

monoquinoid formula does not appear preferable to the biquinoid, and there are various objections to the adoption of Jacobson's formula. 1. There is undoubtedly the closest connection between Gomberg's hydrocarbon and the haloid derivatives of triphenylmethyl, and Baeyer and Villiger have shown that it is improbable that these latter have a quinoid structure. 2. There appears to be no reason for doubting the possibility of the existence of such a hydrocarbon as hexaphenylethane after it has been proved that the derivatives of tetraphenylmethane not only exist but are very stable, and are often formed extremely easily. 3. Finally, the conversion of hexaphenylethane into benzhydryl tetraphenylmethane can be explained by the addition of the elements of a molecule of hydrochloric acid, which leads to the formation of triphenylmethane and triphenylchloromethane, $(\text{C}_6\text{H}_5)_3\text{C} \cdot (\text{C}_6\text{H}_5)_3 + \text{HCl} = (\text{C}_6\text{H}_5)_3\text{CH} + (\text{C}_6\text{H}_5)_3\text{CCl}$, followed by condensation and separation of HCl .—*Berichte*, xxxviii., No. 3.

MEETINGS FOR THE WEEK.

TUESDAY, 30th.—Royal Institution, 5. "Velazquez—The Court Portrait Painter," by the Rev. Henry G. Woods, D.D.

THURSDAY, June 1st.—Royal Institution, 5. (The Tyndall Lecture). "Electromagnetic Waves," by Prof. J. A. Fleming, F.R.S., &c.

Chemical, 8. "Constituents of the Seeds of *Hydnocarpus Wightiana* and of *Hydnocarpus anthelmintica*—Isolation of a Homologue of Chaulmoogric Acid" and "Constituents of the Seeds of *Gynocardia odorata*," by F. B. Power and M. Barrowcliffe. "Relation of Ammonium to the Alkali Metals—A Study of Ammonium-magnesium and Ammonium-zinc Sulphates and Selenates," by A. E. H. Tutton. "Camphorlazoumide," by M. O. Forster and H. E. Pierz. "Influence of Substitution on the Formation of Diazoamines and Aminoazo-compounds—Part III. Azo-derivatives of the Symmetrically Disubstituted Primary Me-a-diamines," by G. T. Morgan and W. O. Wootton. "Diazo-derivatives of Mono-acylated Aromatic Paradiamines," by G. T. Morgan and Miss F. M. G. Micklethwaite. "Significance of Optical Properties as Connoting Structure—Campherquinone, Hydrazones, Oximes—A Contribution to the Chemistry of Nitrogen," by H. E. Armstrong and W. Robertson. "Solubility as a Measure of the Change undergone by Isodynamic Hydrazones—(1) Campherquinone-phenylhydrazones, (2) Acetaldehyde-phenylhydrazones," by W. Robertson. "The Design of Gas-regulators for Thermostats," by T. M. Lowry. "Constitution of Halbaloin," by H. A. D. Jowett and C. E. Potter. "Influence of Substitution on the Formation of Diazoamines and Aminoazo-compounds—Part IV. 5-Bromo-2,4-dimethyl-2:4-diamino-toluene," by G. T. Morgan and A. Clayton. "Action of Hypobromous Acid on Piperazine," by F. D. Chattaway and W. H. Lewis. "Action of Magnesium Methyl Iodide on Pinene Nitroschloride," by W. A. Tilden and J. A. Stokes. "Racemisation Phenomena during the Hydrolysis of Optically Active Menthyl and Bromyl Esters by Alkali," by A. McKenzie and H. B. Thompson.

FRIDAY, 2nd.—Royal Institution, 9. "Personal Recollections of Johannes Brahms," by George Henschel.

SATURDAY, 3rd.—Royal Institution, 3. "Exploration in the Philippines," by A. Henry Savage Landor.

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THE CHEMICAL NEWS.

VOL. XCI., No. 2375.

THE ELECTROLYTIC SEPARATION OF IRON AND ZINC.

By E. G. CURRIE.

ALTHOUGH either of these metals in solution can be determined with comparative accuracy by electrolytic methods, solutions of salts of their double oxalates being the most suitable, owing to the fact that the decomposition-potential of their double oxalate solutions lie very near each other, the estimation, by electrolysis, of the amounts of these metals, in a solution containing both, presents some features of difficulty.

Although the working-potential difference required for the precipitation of either iron or zinc from its double oxalate solution is practically the same, namely, 3.6 to 4.3 volts, if a solution containing both is electrolysed, the two metals do not separate out simultaneously, but zinc with a little iron is first deposited on the cathode.

Classen has found that with the double oxalates of iron and zinc the electrolysis proceeds very satisfactorily, and the united weight of the two metals may readily be determined if there is less than one-third as much zinc as iron in the solution. If the proportion of zinc is greater the zinc re-dissolves with evolution of gas as the action proceeds, a precipitate of oxide of iron being at the same time formed.

Moreover, the deposition of an alloy of iron and zinc on a platinum cathode is attended with the objectionable feature of the difficulty of removing the last traces of zinc from the surface of the platinum.

The united weight of the two metals being determined, they may with difficulty be brought into solution by prolonged heating with strong hydrochloric or sulphuric acid, the iron being afterwards titrated with stannous chloride or potassium permanganate.

Vortmann proposes the following methods:—

I. Four to six grms. of potassium sodium tartrate and an excess of 10 to 20 per cent solution of sodium hydroxide are added to the solution of the metals, and the liquid is electrolysed at a potential-difference of 2 volts with a current-strength of 0.07 to 0.1 ampère. It is best to raise the temperature at the close of the operation to 50–60°. After several hours the iron will be precipitated, the zinc remaining in solution. The zinc can then be quantitatively precipitated by electrolysis with a potential-difference of 4 volts.

II. Potassium cyanide is added to a solution of both metals, till the first formed precipitate is just re-dissolved, and then sodium hydroxide in order to have the iron in the form of sodium ferrocyanide, which is not decomposed by the current in the presence of free alkali. Too large an excess of cyanide hinders the separation. The current-density required is 0.3 to 0.6 ampère.

Recently, Holland and Bertiaux have recommended the following (*Bull. Soc. Chim. Abstr.*, 1903, ii., 513):—

An addition of 25 to 50 c.c. sulphurous acid to a solution of the sulphates of the two metals, which is then nearly neutralised with sodium hydroxide, 15 c.c. of a 20 per cent solution of potassium cyanide is added, and then 50 c.c. of a sodium hydroxide solution of specific gravity 1.11, the whole being diluted to 300 c.c., is electrolysed cold with a current of 1 ampère.

Both these last methods are open to the objection that the deposited zinc always contains traces of iron, sometimes as much as 0.039 to 0.103 grm.

EXPERIMENTAL.

I. With Acetaldehyde.

Using a platinum-dish (capacity about 200 c.c.) as cathode, and a platinum anode, either of the disc or bucket shape, a thin layer of copper or silver being first of all deposited on the cathode in order to obviate the disadvantage of having zinc deposited directly on the platinum, experiments were conducted on the lines of these last two methods, on the suitability as a reducing agent of acetaldehyde in varying amounts instead of a solution of sulphurous acid, in the hope of obtaining zinc alone deposited on the cathode. Experiments were also made with solutions of the double oxalates of the two metals, with the addition of varying amounts of acetaldehyde in order to keep the iron in the ferrous state, in the hope of obtaining both metals simultaneously deposited on the cathode.

Many experiments of this nature proved very unsatisfactory, both as regards the nature of the metallic deposition, whether deposited on a copper or silver covered cathode, and also owing to the ease with which aldehyde resin was formed, very unsuitable for electrolytic determinations; any increase in the E.M.F. or rise in temperature being sufficient to produce it, sometimes in considerable amount.

II. With Hydrazine Sulphate.

Hydrazine sulphate, as not being likely to produce any deleterious effects, having been tried as a reducing agent in the presence of the ammonium double oxalates of the two metals, the results, although much better than with aldehyde, were uncertain; a further difficulty being also experienced because, owing to the readiness of the solutions prepared for electrolysis to crystallise, only small amounts of the iron and zinc salts could be taken. After many experiments, with no very definite results, this reducing agent was abandoned.

III. With Hydroxylamine Sulphate.

This salt being more soluble than hydrazine sulphate, the solutions prepared for electrolysis did not so readily form crystals, and more satisfactory results were obtained than with either hydrazine sulphate or aldehyde. On electrolysis ammonium oxalate solutions of the two metals containing varying amounts of hydroxylamine sulphate, in most cases metallic deposition took place at once, but the deposition had a great tendency to re-dissolve after the electrolysis had proceeded up to a certain point. The electrolyte very rapidly became alkaline, even although the effect was tried of adding during electrolysis, drop by drop, from a burette a cold saturated solution of oxalic acid or a strong solution of tartaric acid.

In order to obtain with certainty from solutions of the double oxalates deposits of zinc in dense metallic form, it is necessary to keep the solution acid during electrolysis (Classen, *Zeit. f. Electro-chemie*, 1894, i., 280).

Also, in a too alkaline electrolyte a precipitate of iron hydroxide may form.

It was at length found that with an electrolyte formed by adding a solution of about 1 grm. of the sulphates of the two metals to an ammonium oxalate solution containing not more than 1 grm. hydroxylamine sulphate, the addition of 10 c.c. of a cold saturated solution of oxalic acid, and the employment of a large amount of a saturated solution of oxalic acid during electrolysis, it was possible in some cases to obtain a fairly complete deposition of iron and zinc on the silver covered cathode, in spite of the fact of the electrolyte becoming more and more alkaline during the electrolysis.

This method, however, was unreliable, the solution invariably being somewhat turbid at the end of the experiment. It was also found that the addition of more than 10 c.c. of a cold saturated solution of oxalic acid to the solution before electrolysis had the effect of delaying the deposition for a time. Tartaric acid being less readily decomposed by the electric current than oxalic, the effect

of adding a 20 per cent solution of the former acid to the electrolyte during the experiment was tried, with better results; the electrolyte, as formerly, consisting of a solution of the double oxalate salts of the two metals containing 1 grm. hydroxylamine sulphate, together with 10 c.c. of a cold saturated solution of oxalic acid.

It was also found that the addition of not more than 0.5 grm. hydroxylamine sulphate was more satisfactory than a larger amount.

The addition of a 20 per cent solution of tartaric acid to the electrolyte during electrolysis instead of a saturated solution of oxalic acid was likewise found to have a marked influence on the character of the deposited metal; the deposit being firm, crystalline in appearance, grey in colour, not dark and powdery as was so often the case with oxalic acid.

Experiments were also made with electrolytes containing 2 c.c. of a 20 per cent solution of tartaric acid instead of 10 c.c. of a saturated solution of oxalic acid, with equally good results. The addition, however, of more than 2 c.c. of the tartaric acid solution results in a dark loose deposit, showing a tendency to re-dissolve in the electrolyte during electrolysis.

It was found, as the result of several experiments, that by the use of tartaric in place of oxalic acid during electrolysis, the solution remained clear throughout, reliable results being obtained under the following conditions:—

1. The addition of at least 20 c.c. of the tartaric acid solution to the electrolyte during electrolysis.

2. Provided that the proportion of zinc to iron is not too high, and that not more than 1 grm. of the two salts is taken. (Ferrous ammonium sulphate and zinc sulphate being the salts used).

The larger the ratio of zinc to iron the harder it is to obtain a complete metallic deposition, the zinc after a certain time re-dissolving in the electrolyte.

The deposited metals not being readily soluble in sulphuric or hydrochloric acids, but easily soluble in nitric acid, the combined deposits of silver, iron, and zinc were dissolved off the cathode by heating with nitric acid; a large excess of ammonia was then added; the solution heated for some time, and the ferric hydroxide thus obtained filtered, washed with hot ammonia solution to remove traces of silver and zinc, dissolved in dilute sulphuric acid, and added to a solution of 6 grms. ammonium oxalate in 100 c.c. water, the total volume being made up to about 160 c.c. On electrolysis this solution a complete deposition of the iron was not obtained.

In another experiment, on making the solution just alkaline with ammonia, a better but still unsatisfactory result was obtained.

On dissolving the iron hydroxide in oxalic acid, adding the solution to a hot solution of 4 grms. ammonium oxalate in 50 c.c. water, and adding ammonia till just alkaline, better results were obtained, but much gas was evolved during electrolysis; it was also difficult to keep the volume of the electrolyte within reasonable limits without evaporating it down.

On dissolving the iron hydroxide in about 5 grms. oxalic acid, adding ammonia till just alkaline (total volume about 160 c.c.), a complete separation of iron was obtained by electrolysis.

Conditions for Analysis.

Metals present as sulphates. Substance added: 6 to 8 grms. ammonium oxalate, 0.5 grm. hydroxylamine sulphate, 2 c.c. 20 per cent tartaric acid or 10 c.c. cold saturated oxalic acid. Total volume of solution, 150 to 160 c.c. Room temperature. Current-density at cathode, 1 to 2 amperes. Potential-difference between electrodes 4.6 to 4.9 volts.

Experiment I.

Used: 0.4184 grm. $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, 0.6240 grm. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 6 grms. ammonium oxalate, 1 grm. hydroxylamine sulphate, 10 c.c. cold saturated solution of

oxalic acid. Volume of solution, 150 to 160 c.c. About 50 c.c. cold saturated solution of oxalic acid added during electrolysis.

Temperature, room. Time, 3½ hours.

Volts.	Ampères.
4.2	0.95
5.0	2.35
5.1	2.25

Platinum dish + Ag, Fe, and Zn.. 38.1828

Dish + Ag 37.9816

Fe + Zn 0.2012

Result.—Per cent Fe, Zn.

Found 19.301

Theory.. .. . 19.288

Difference +0.013

Experiment II.

Used: 0.5070 grm. $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, 0.6212 grm. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 6 grms. ammonium oxalate, 0.5 grm. hydroxylamine sulphate, 10 c.c. cold saturated solution of oxalic acid. Volume of solution, 150 to 160 c.c. About 35 to 40 c.c. of a 20 per cent solution of tartaric acid added during electrolysis.

Temperature, room. Time, 5 hours.

Volts.	Ampères.
4.1	0.80
4.3	1.10
4.8	1.60

Platinum dish + Ag, Fe, and Zn.. 38.7808

Dish + Ag 38.5684

Fe + Zn 0.2124

Result.—Per cent Fe, Zn.

Theory.. .. . 18.879

Found 18.826

Difference -0.053

Experiment III.

Used: 0.4568 grm. $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, 0.5582 grm. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 6 grms. ammonium oxalate, 0.5 grm. hydroxylamine sulphate, 10 c.c. cold saturated solution of oxalic acid. Volume of solution, 150 to 160 c.c. About 5 to 6 c.c. of a 20 per cent solution of tartaric acid added during electrolysis.

Temperature, room. Time, 3 hours.

Volts.	Ampères.
4.6	1.30
4.8	1.40

Platinum dish + Ag, Fe, and Zn.. 37.3172

Dish + Ag 37.1236

Fe + Zn 0.1936

Result.—Per cent Fe, Zn.

Found 19.073

Theory.. .. . 18.876

Difference +0.197

The deposit of Fe, Zn, Ag dissolved in nitric acid, a considerable excess of ammonia added, the ferric hydroxide filtered, washed with hot dilute ammonia, dissolved in oxalic acid, added to a solution of 3 grms. ammonium oxalate in 40 c.c. water. The solution then made alkaline with ammonia and electrolysed.

Temperature, room. Time, 2½ hours.

Volts.	Ampères.
4·2	1·90
4·4	1·80

Result.

	Iron, FeSO ₄ (NH ₄) ₂ SO ₄ ·6H ₂ O.	Zinc, ZnSO ₄ ·7H ₂ O.
	Per cent.	Per cent.
Found	14·667	22·680
Theory	14·285	22·648
Difference ..	+0·382	+0·032

Experiment IV.

Used: 0·3816 gm. FeSO₄(NH₄)₂SO₄·6H₂O, 0·502 gm. ZnSO₄·7H₂O, 6 grms. ammonium oxalate, 0·5 gm. hydroxylamine sulphate, 10 c.c. cold saturated solution of oxalic acid. Volume of solution, 150 to 160 c.c. About 17 to 18 c.c. of a 20 per cent solution of tartaric acid added during electrolysis.

Temperature, room. Time, 3½ hours.

Volts.	Ampères.
4·7	1·05
4·8	1·35
4·9	1·65

Platinum dish + Ag, Fe, and Zn..	37·7678
Dish + Ag	37·5792

Fe + Zn 0·1886

Result.—Per cent Fe, Zn.

Found	19·609
Theory	19·328

Difference +0·281

The deposit of Ag, Fe, and Zn dissolved in nitric acid, a large excess of ammonia added, heated, filtered, the precipitate washed with hot ammonia solution, dissolved in as little as possible oxalic acid, added to a solution of 2 grms. ammonium oxalate in 30 c.c. water, made alkaline with ammonia, and electrolysed.

Temperature, room. Time, 3½ hours.

Volts.	Ampères.
4·2	1·90
4·6	1·75

Result.

	Iron, (FeSO ₄ NH ₄) ₂ SO ₄ ·6H ₂ O.	Zinc, (ZnSO ₄) ₇ H ₂ O.
	Per cent.	Per cent.
Found	14·517	22·957
Theory	14·285	22·648
Difference ..	+0·232	+0·309

Experiment V.

Used: 0·4768 gm. (FeSO₄NH₄)₂SO₄·6H₂O, 0·2376 gm. ZnSO₄·7H₂O, 7 grms. ammonium oxalate, 0·5 gm. hydroxylamine sulphate, 2 c.c. of a 20 per cent solution of tartaric acid. Volume of solution, 150 to 160 c.c. About 44 c.c. of the tartaric acid solution added during electrolysis.

Temperature, room. Time, 3½ hours.

Volts.	Ampères.
4·7	1·10
4·6	1·35
4·9	1·60

Platinum dish + Ag, Fe, and Zn..	36·9712
Dish + Ag	36·8504

Fe and Zn 0·1208

Result.—Per cent Fe, Zn.

Theory	17·063
Found	16·909

Difference -0·154

Experiment VI.

Used: 0·5362 gm. FeSO₄(NH₄)₂SO₄·6H₂O, 0·5928 gm. ZnSO₄·7H₂O, 8 grms. ammonium oxalate, 0·5 gm. hydroxylamine sulphate, 2 c.c. of a 20 per cent solution of tartaric acid. Volume of solution, 150 to 160 c.c. A 20 per cent solution of tartaric acid added, drop by drop, during the electrolysis.

Platinum dish + Ag, Fe, and Zn..	37·7412
Dish + Ag	37·5282

0·2130

Result.—Per cent Fe, Zn.

Found	18·866
Theory	18·662

Difference +0·204

Experiment VII.

Used: 0·4864 gm. FeSO₄(NH₄)₂SO₄·6H₂O, 0·3746 gm. ZnSO₄·7H₂O, 6 grms. ammonium oxalate, 0·5 gm. hydroxylamine sulphate, 2 c.c. of a 20 per cent solution of tartaric acid. Volume of solution, 150 to 160 c.c. About 33 c.c. of a 20 per cent solution of tartaric acid run in during electrolysis.

Temperature, room. Time, 3½ hours.

Volts.	Ampères.
4·8	1·30
4·6	1·30
4·8	1·35

Platinum dish + Ag, Fe, and Zn..	37·6352
Dish + Ag	37·4802

Fe and Zn 0·1550

Result.—Per cent.

Found	18·002
Theory	17·909

Difference +0·093

The deposit of Ag, Fe, and Zn dissolved in nitric acid, a large excess of ammonia added, heated, filtered, the hydroxide washed with hot dilute ammonia, dissolved in 4 to 5 grms. oxalic acid, made just alkaline with ammonia, and electrolysed.

Temperature, room. Time, 3½ hours.

Volts.	Ampères.
4·5	0·45
4·5	0·45

Result.—Per cent.

	Theory.	Found.	Difference.
Iron	14·285	14·062	-0·223
Zinc	22·648	23·117	+0·469

Experiment VIII.

Used: 0·3456 gm. FeSO₄(NH₄)₂SO₄·6H₂O, 0·4028 gm. ZnSO₄·7H₂O, 8 grms. ammonium oxalate, 0·5 gm. hydroxylamine sulphate, 2 c.c. of a 20 per cent solution of tartaric acid. Volume of solution, 150 to 160 c.c. About 41 to 43 c.c. of a 20 per cent tartaric acid solution run in during electrolysis.

Temperature, room. Time, 3½ hours.

Volts.	Ampères.
4·7	1·30
4·8	1·75
4·9	1·90

Platinum dish + Ag, Fe, and Zn..	37·8394
Dish + Ag	37·6980

0·1414

Result.—Per cent Fe, Zn.

Found	18.893
Theory	18.773
	+0.120

The deposit of Ag, Fe, and Zn dissolved in nitric acid, a large excess of ammonia added, heated, filtered, the hydroxide washed with hot ammonia solution, dissolved in 5 grms. oxalic acid, made just alkaline with ammonia, and electrolysed.

Temperature, room. Time, 3½ hours.

Volts,	Ampères.
4.5	0.55
4.5	0.75

Result.—Per cent.

	Found.	Theory.	Diff.
Iron, $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$.	14.583	14.285	+0.298
Zinc, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	22.591	22.648	-0.057

Experiment IX.

Used: 0.4780 gm. $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, 0.4528 gm. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 8 grms. ammonium oxalate, 0.5 gm. hydroxylamine sulphate, 10 c.c. cold saturated solution of oxalic acid. Volume of solution, 150 to 160 c.c. During electrolysis, about 34 c.c. of a 20 per cent solution of tartaric acid added.

Temperature, room. Time, 3¾ hours.

Volts.	Ampères.
4.7	0.95
4.8	1.40
5.0	1.40

Platinum dish + Ag, Fe, and Zn..	37.8724
Dish + Ag	37.7003

Fe and Zn	0.1716
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Result.—Per cent Fe, Zn.

Found	18.435
Theory	18.339

Difference	+0.096
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The deposit of Ag, Fe, and Zn dissolved in nitric acid, a large excess of ammonia added, heated, filtered, the precipitate washed with hot ammonia solution, dissolved in about 5 grms. oxalic acid, made just alkaline with ammonia (total volume about 160 c.c.), and electrolysed.

Temperature, room. Time, 3½ hours.

Volts.	Ampères.
4.5	1.90
4.5	1.15

Result.—Per cent.

	Found.	Theory.	Difference.
Iron	14.602	14.285	+0.317
Zinc	22.482	22.648	-0.166

Conclusion.

By the use of hydroxylamine sulphate as a reducing agent in the presence of the sulphates of iron and zinc, it is possible, under certain conditions, to obtain by electrolysis an alloy of the two metals suitable for quantitative determination, provided that the ratio of zinc to iron is not more than 2.4 to 1.

The cathode should be first of all covered with a layer of silver; this can be easily done by electrolytically depositing from a solution of silver cyanide.

The determination is conducted as follows:—

About 1 gm. ferrous ammonium sulphate and zinc sulphate is dissolved in about 20 c.c. water, with the addition of one drop dilute sulphuric acid.

From 6 to 8 grms. ammonium oxalate and about 0.5 gm. hydroxylamine sulphate is dissolved in 100 c.c.

water; the solution of the two metals is slowly poured in, and then 2 c.c. of a 20 per cent solution of tartaric acid, or 10 c.c. of a cold saturated solution of oxalic acid is added with constant stirring, and the whole made up to about 150—160 c.c. with water.

On the electrolyte beginning to turn red and alkaline, which takes place after twenty minutes to one-half hour's electrolysis, a 20 per cent solution of tartaric acid is slowly added, drop by drop from a burette, till the deposition is complete, which takes place in about three to three and three-quarter hours' time; about 35 to 40 c.c. should be used, the electrolyte at the end of the experiment being alkaline and red in colour.

After the reduction is completed (this is best determined by acidulating a small quantity of the solution with hydrochloric acid and adding potassium ferrocyanide), the deposit is washed with water without interrupting the current, then with a little alcohol, heated on a triangle over asbestos till the alcohol has just evaporated, cooled in a desiccator, and weighed.

In order to determine the percentage of iron, the deposit of silver, iron, and zinc (after weighing) is dissolved in hot nitric acid, heated, a considerable excess of ammonia added, the ferric hydroxide is then filtered, and the precipitate washed with hot dilute ammonia till the washings are free from traces of silver and zinc. The filter and precipitate is then removed from the funnel, placed in a small beaker or porcelain dish containing a hot solution of about 5 grms. oxalic acid in about 40 c.c. water, and heated till the precipitate is dissolved. Any residue of ferric hydroxide remaining behind in the beaker after filtration is also dissolved in a little oxalic acid, and the whole filtered and made just alkaline with ammonia. The solution is made up to about 160 c.c., and electrolysed in the ordinary way. The dish with its deposit of iron being then weighed, the percentage of zinc may be determined by difference.

ON A NEW TYPE OF ELECTRIC FURNACE, WITH A RE-DETERMINATION OF THE MELTING-POINT OF PLATINUM.*

By J. A. HARKER, D.Sc., Joule Scholar of the Royal Society,
Assistant at the National Physical Laboratory, Teddington.

I. Preliminary Discussion. Use of Oxides at High Temperatures, &c.

AN investigation is now in progress in the thermometric department of the National Physical Laboratory, having for its object the design of an electrical method of measuring temperatures from 1200° C. upwards in some such way as temperatures below this value may now be determined by an appropriate thermocouple or resistance thermometer. It is, of course, common knowledge that metals such as platinum and alloys of the platinum group are unable for prolonged periods to withstand, without alteration of their structure and properties, the effects of temperatures above about 1200° C., particularly if in presence of even small quantities of certain gases, such as are very difficult to ensure shall be completely absent, especially at the higher ranges. This is the case with nearly all methods of heating, whether electrical or otherwise.

The brilliant researches of Moissan on the stability of all kinds of substances at very high temperatures, and the recent work of Nernst culminating in the invention of his well-known lamp, in which the light-giving filament is formed of a complex mixture of oxides of rare earths, directed the attention of the author to this class of bodies. From a study of their behaviour he has been able to work out a method of attaining by very simple means very high temperatures, which may be controlled with great ease.

* A Paper read before the Royal Society, April 13, 1905.

In order, therefore, to avoid the necessity of having contacts on the tubes capable of carrying relatively large

Nernst himself mentions the idea of using a tube, and H. N. Potter, in 1902, took out American patents for a



Fig. 1 shows the arrangement adopted in the small type of vertical furnace used in the experiments detailed later. AB is the central conducting tube, which in this case was

about 10 m.m. internal diameter and 60 to 70 m.m. long. *cd* is a tube of hard porcelain or other suitable refractory material 30 to 40 m.m. internal diameter, on which is wound the heating spiral of nickel wire, protected from oxidation by some suitable means. The space between is filled with powdered zirconia, which should not contain any appreciable admixture of any other substance, otherwise it gradually becomes a conductor at very high temperatures. When the furnace is in action, in this layer of zirconia there is a falling gradient of temperature from the centre outwards, which suffices to prevent the nickel spiral from becoming unduly heated by radiation from the inner tube. The current is led into the tube by platinum flexibles, enveloping it at *A* and *B* and joined by autogen soldering to nickel or platinum wires leading to suitable terminals.

To a similar pair of terminals on the nickel wire heating circuit is connected an appropriate source of current with regulator and ammeter.

To enable the tube to be heated fairly uniformly to above the upper electrode, it is sunk 20 or 30 m.m. below the level of the top of the nickel spiral, and a mouth-piece of rather wider unglazed porcelain tubing is slipped over its upper end, which can be closed if necessary by a stopper. A capillary tube, made of the same mixture as the furnace tube proper, may be fitted below for the introduction of any gas desired.

To light up such a furnace current sufficient to dissipate 100 to 300 watts is passed through the nickel spiral, the safe maximum amount of energy supplied during the heating up of furnace depending on the details of construction and the nature of the protecting medium in which the nickel is buried. As a rule, less than half-an-hour suffices to bring the central tube to a red heat. The terminals of the tube are meanwhile connected to the supply of current at from 200 to 500 volts.* Since the temperature coefficient of practically all solid electrolytic conductors is negative and very large, the current in them becomes unstable at very high temperatures, unless a sufficient steadying resistance is always left in series with them. For furnace work it suffices if 20 to 25 per cent of the whole volts of the circuit are dropped on the series resistance.

Care should be taken with furnaces run for long periods at very high temperatures that the temperature of the electrodes does not rise beyond the melting-point of platinum. Though this is easily arranged for in the design of small tube furnaces, it becomes more difficult to ensure in those of larger size. In these the conductor is arranged in the form of a reel, the electrode wires wound round the wider part at the ends being thus more easily kept relatively cool.

IV. Use of Furnace for Melting-point Determinations.

In the type of furnace just described, when about 150 joules are generated in the jacket circuit, a current of about 2 amperes suffices to take the central portion to about 2000° C., the volts dropped on the tube depending on the distance between the electrodes and the condition of the tube material, but rarely exceeding 100 volts at the higher temperatures, and often being only 60 or 80 volts. It was found that with a well-designed regulating resistance, the control of the temperature of the inner walls of these surfaces was so perfect between 800° and 2000° C., that well-defined melting-points could be obtained in them on very small quantities of substance. Using a suitably supported thermo-junction of bare platinum, with platinum-rhodium or platinum-iridium, it was found possible, even with fairly rapid heating, to obtain very concordant values for the melting-point of the platinum wire forming the junction. It was further obvious that, if the melting-point of platinum were accurately known, this method would furnish an excellent and easily determined high temperature fixed point for the thermo-junction standardisation.

* Short furnaces can be lit up on a 100-volt circuit.

V. Thermo-junctions Used and their Standardisation.

Having in the laboratory a considerable number of specimens of platinum and platinum alloys of different composition from different sources, some of which had been accurately studied as thermo-junctions over a large range, a selection was made from these of a number of characteristic specimens, giving widely different electromotive forces, and the formula connecting the thermo-electromotive force with temperature was carefully determined for each. In most cases this was done by direct comparison in a specially arranged electric furnace with the laboratory standards, from somewhat below 400° C. to over 1250° C. In certain other cases the standardisation was made by means of selected fixed points. The details of these methods of standardisation and of the potentiometer used, which was specially designed for thermo-electric work, were described in the author's earlier paper on the "High Temperature Standards of the National Physical Laboratory," published in the *Phil. Trans.* for 1904, vol. cciii., pp. 348 to 384. As a measure of the accuracy attained it will suffice to say that the coefficients for the type of formula—

$$Et = -\alpha + \beta t + \gamma t^2,$$

were calculated by least squares for each junction from the observations made, and that in a comparison of six junctions with two standards embracing 10 to 12 temperatures spaced fairly regularly between 400° and nearly 1300° C., it was seldom that the difference between the observed values of the E.M.F. of any junction at any point, and the value of the E.M.F. for that temperature calculated from the formula, differed by as much as 1° C., and in no single case exceeded 2° C.

The type of formula chosen is the same as is given in the paper previously referred to, and the scale of temperature adopted is the one there defined, which was shown to agree within the limits of error with the scale of temperature used at the Reichsanstalt, as established by the experiments of Holborn and Day. Below 300° C. a formula of this kind having a term which does not vanish when $t=0$, does not represent the E.M.F. exactly, since from about this temperature downwards there is a marked change in the curve of E.M.F. for all junctions made of the platinum metals, and on this account, therefore, it is not permissible to use any of these formulæ for downward extrapolation except over quite a limited range.

(Professor Callendar, in his article on thermo-electricity in the supplementary volumes of the "Encyclopædia Britannica," says:—"Holborn and Day have gone back to Tait's method at high temperatures employing arcs of parabolas for limited ranges. But since the parabolic formula is certainly erroneous at low temperatures, it can hardly be trusted for extrapolation above 1000° C." The results given later seem, however, to render it highly probable that, contrary to expectation, upward extrapolation is justifiable).

VI. Method of Experiment.

The experiments with each junction were made as follows:—The two wires selected were melted together in a small oxidising oxyhydrogen flame, and after cooling, the whole was mounted on a convenient insulating stand with fine adjustments. The "hot" junction was brought to a central position in the heated furnace at an appropriate height, and the two "cold" junctions were placed in glass tubes in ice.

The observer then followed the rise of E.M.F. on the potentiometer, while an assistant gradually increased the furnace current as required. When the melting-point of platinum was reached, if the rate of rise were not very much too rapid, an exceedingly well marked halt was obtained. During the halt, the duration of which depended of course on the rate of heating of the furnace, one of three things usually happened, the particular phenomenon observed depending on the relative position, diameter, and state of tension of the wires forming the thermo-couple.

Either, first: The wires sprang away from one another,

one of them usually coming into contact with the side of the tube. The moment when this occurred was always easily recognisable on the potentiometer.

Or secondly:—A globule of molten platinum formed on the end of the wires. This sometimes attained such dimensions as to drop off, thereby breaking contact.

Or possibly, third:—The globule of platinum formed gradually climbed up the rhodio-platinum or iridio-platinum wire, to a higher position in the furnace. During its movement, small temperature oscillations are observed on the potentiometer, amounting to perhaps 2° or 3° . The molten platinum did not appear to sensibly attack the other wire, any irregularities on its surface being practically as sharply marked after the experiment as before it, and its total length remaining unaffected.

Provided the furnace wall near the junction were nowhere allowed to rise beyond the melting-point of the platinum-rhodium or platinum-iridium wire (which with 10 per cent alloys is in each case much above that of the pure metal), the temperature attained by the drop of molten platinum, whichever of the above alternatives happened, was very steady and independent of the current in the furnace. There was usually no difficulty in repeating the setting of the potentiometer-slider for the same junction without looking at it, to less than 1° C. if the conditions are not greatly changed. Provided the immersion in the furnace is sufficient, and that there is an ascending gradient of temperature from the furnace mouth downwards, varying the immersion considerably makes no difference in the point of balance attained. After having had the method once explained, an observer not familiar with the apparatus, who was quite unprejudiced as to what value of the thermal force or temperature to expect, was able at once to take an observation, agreeing to within about 2° C. of the mean value previously obtained from a number of experiments with the junction in question.

(To be continued).

THE USE OF QUARTZ UTENSILS IN THE LABORATORY.

By F. MYLIUS and A. MEUSSER.

IN 1903 the firm of W. C. Heraeus placed at the disposal of the Reichsanstalt various quartz utensils, the examination of which, from a chemical point of view, gave the following results:—

1. Water does not attack the vitrified quartz at ordinary temperatures, nor has it any appreciable effect at 100° ; no silicic acid appears to be dissolved.

"The electric conductivity of the water was as little influenced by the walls of the vessel, or by purified quartz glass powder which was introduced, as by 'insoluble silicic acid.' Even continued digestion at 80° (the sulphuric acid produced from the Bunsen burner being meanwhile carefully removed) had no appreciable effect. Thus, for the purpose of purifying water it may be boiled in a quartz flask, the carbon dioxide being thus expelled. The conductivity then decreases, for example, to 0.72×10^{-6} ."

"A striking tendency to retard the boiling is manifested; the flask must from time to time be shaken powerfully, in order to make it boil without expelling the precipitate violently."

(This extract relating to F. Kohlrausch's experiments is taken from the "Report of the Phys.-Tech. Reichsanstalt" for 1903, *Zeit. f. Instrum.*, 1904, 176. For the reference to pulverised "insoluble silicic acid" cf. Kohlrausch and Rose, *Wied. Ann.*, 1893, 1, 133).

2. Caustic soda, caustic potash, ammonia, and solutions of salts which have an alkaline reaction dissolve silicic acid, as might be expected. The effect becomes apparent at very low temperatures, but is much more pronounced on warming, as shown in the accompanying consecutive series of experiments.

3. After baryta-water had been kept at 18° for six months in a quartz vessel from which the air was excluded, small prismatic crystals were formed on the walls. These crystals were decomposed by dilute hydrochloric acid without any evolution of gas, gelatinous silicic acid being separated; thus they consist of barium silicate (cf. Jordis and Kanter, *Zeit. Anorg. Chem.*, 1904, xlii., 418).

4. Dilute acids, with the exception of hydrofluoric acid, do not perceptibly attack quartz, either at the temperature of the room nor at 100° .

5. Concentrated sulphuric acid has no appreciable effect either at 18° or at 100° .

6. Phosphoric acid has no effect at 18° . On concentrating in a quartz dish above 400° , a chemical reaction occurs, giving rise to powerful corrosion, and the separation of white silicic phosphate.

7. Hydrofluoric acid acts as a powerful solvent.

8. Quartz vessels absorb potash from 30 per cent caustic potash; this potash cannot be brought into solution by repeated washing with cold water, but may be dissolved by boiling. Its presence may be shown by means of red

Quartz Flask: Contents, 78 c.c.; Surface covered by Liquid, 89 sq. c.m.

Expt. No.	Reagent.	Time of contact.	Temperature.	Decrease of weight M.grms.*
1.	Water	Several days	$18-100^{\circ}$	0
2.	10 per cent ammonia solution	Two days	18°	0.8
3.	10 per cent caustic soda	"	18°	0.4
4.	30 per cent caustic soda	"	18°	0
5.	30 per cent caustic potash	Four days	18°	1.2
6.	2 N caustic soda	Three hours	100°	48.4
7.	2 N sodium carbonate	"	100°	12.4
8.	2 N caustic potash	"	100°	31.0
9.	2 N caustic soda	"	100°	33.4
10.	2 N sodium carbonate	"	100°	8.4
11.	2 N caustic potash	"	100°	64.2
12.	2 N caustic soda			
13.	N. caustic soda			
14.	N. caustic soda	Fourteen days	18°	2
15.	N. sodium carbonate	"	18°	1.8
16.	Saturated baryta-water	"	18°	0.6
17.	Saturated sodium phosphate	"	18°	0
18.	N. phosphoric acid	"	18°	0
19.	10 per cent ammonia	"	18°	0
20.	25 per cent ammonia	Sixty days	18°	0
21.	25 per cent ammonia	Six hours (re-filled four times) ..	Up to 60°	2.6

Total loss of flask = 207.2 m.grms.

No corrosion of the flask could be observed; the walls appeared to the eye as smooth as in a new flask.

* A possible error of ± 0.2 m.grm. might occur in the weighings; accurate weighings in Expts. 4 and 16—19 would have given a decrease.

laccoid solution, which is coloured blue by the potash extracted. With 30 per cent caustic soda solution, no absorption is observed under the same conditions.

9. Quartz vessels have the power of absorbing certain dyes from their solutions. This was observed, for example, on standing for 24 hours in contact with aqueous solutions of methylene blue (*cf.* G. Quincke, *Ann. d. Phys.*, 1902, [4], vii., 74), Congo red, and rhodamine, with alcoholic solution of aniline blue, and with ethereal solution of iodo-eosin (containing some moisture).

(The absorption of iodo-eosin by quartz is of a decidedly smaller order of magnitude than that produced by the alkali of glass).

The quantities of the dyes absorbed are extremely small; they adhere to the walls after washing as a uniformly coloured crust, and may be removed again by hot solvents.

The examination of the question whether and how far the power possessed by vitrified quartz of absorbing certain substances also extends to solvents, and especially to water, requires exceedingly careful experiments.

The increasing application of quartz vessels in the laboratory is caused chiefly by the fact that the material is fireproof, and resists changes of temperature. The use of quartz tubes for various physical purposes is well known. As an example of their use in analytical chemistry, may be mentioned the ignition tubes for arsenic determination by Stas' method, for which the infusible quartz is specially suited. But naked gas flames readily produce an increasing corrosion of the quartz, which somewhat limits its use.

Secondly, the chemical homogeneity of the material, its indifference to causes which produce decay, and its chemical resistance to water are all advantages.

Thus, quartz vessels may readily be used for accurate chemical work with neutral or acid aqueous solutions in which a contamination with alkali might occur with glass vessels.

On the other hand, by the preceding observations it is confirmed that quartz possesses no advantage over glass as regards alkaline liquids, since in both cases solid matter goes into solution.

In more accurate work we are, as heretofore, obliged to employ the rare metals, the use of which also in experiments with hydrofluoric acid and various fluxes seems unavoidable.

Vessels of moulded quartz, as compared with porcelain, possess the advantage of being transparent.—*Zeit. für Anorg. Chem.*, 1905, xliv., 221.

PROCEEDINGS OF SOCIETIES.

FARADAY SOCIETY.

Ordinary Meeting, Thursday, May 18th, 1905.

Dr. F. MOLLWO PERKIN, Treasurer, in the Chair.

Dr. T. MARTIN LOWRY read a paper entitled "*An Application to Electrolytes of the Hydrate Theory of Solutions.*"

The object of the paper is to consider the possibility of extending the hydrate theory to electrolytes in such a way as to take account of the observations which form the experimental basis of the theory of electrolytic dissociation. The hydrate theory postulates that an aqueous salt solution consists of a mixture of hydrates in equilibrium with the solvent and with one another. But it must be supposed that even in solution there is a limit to the possibility of hydrate formation, so that ultimately a stage will be reached at which the molecule as such will be unable to combine with any further quantity of water. The ionisation of an aqueous electrolyte consists essentially in a further process of hydration whereby the fully hydrated molecule combines with an additional quantity of water to

form two or more hydrated ions. The hydration of the ions is thus conceived to be the primary cause of the ionisation of aqueous electrolytes. It is believed that this extension of the hydrate theory to the phenomena of electrolysis may help to remove the fundamental difficulty of Arrhenius's theory, namely, the absence of a *motive* for electrolytic dissociation.

The evidence in support of the hydrate theory of ionisation is summarised as follows:—

1. The theory is in accord with the fact that the best "ionising" solvents are those which are themselves most highly associated. Whilst Arrhenius laid special stress on dissociation as the characteristic feature of the process of ionisation, the hydrate theory emphasises an association of solvent and solute which is the primary cause of the separation of the ions. Such an association with the solute may be expected to occur most readily in the case of solvents composed of molecules having a high coefficient of association.

2. Complete ionisation is possible only in presence of a very large excess of water, that is, under exactly those conditions which are most favourable to the formation of complex hydrates.

3. The influence of temperature on ionisation is also in accord with the view that the process is essentially one of association with the solvent.

4. Evidence in favour of the hydrate theory of ionisation is afforded by a consideration of the mobilities of the different ions in aqueous solutions. In the following table of ionic mobilities—

Li.	Na.	K.	Rb.	Cs.
33.44	43.55	64.67	67.6	68.2

the larger atoms yield the more mobile ions; the lithium ion (at. wt. 7) moves through the solution only half as rapidly as the rubidium ion (at. wt. 85), or the caesium ion (at. wt. 133). Such a result strongly supports the view that in aqueous solutions the ions are present in the form of complex hydrates.

5. The mobility of the hydroxyl ion is more than double as great as that of any other anion; whilst that of the hydrogen ion is nearly five times as great as that of any other cation. The peculiar properties of these two ions are most readily explained by supposing that they are either anhydrous or are combined with a smaller proportion of water than any of the other ions. Confirmation of this view is afforded by at least two independent considerations:

i. The affinity of water molecules for the ions H and OH must be relatively slight, since otherwise liquid water, like fused salt or caustic soda, would be a good electrolyte.

ii. Whereas nearly all sodium and potassium salts are good conductors, the acids from which they are derived are often exceedingly poor conductors.

6. Independent evidence in favour of the hydrate theory of ionisation is to be found in a consideration of the freezing-points of dilute aqueous solutions. At extreme dilutions the molecular depression of the freezing-point reaches a maximum value corresponding very closely with that required by the theory of electrolytic dissociation. In less dilute solutions, however, values are obtained which cannot be accounted for in terms of this theory as originally propounded, but which are explicable if, as the hydrate-theory assumes, part of the solvent is removed as far as freezing-point lowering is concerned.

7. The theory of electrolytic dissociation owes much of its acceptability to the readiness with which it lends itself to exact mathematical treatment. The whole theory can indeed be summed up in the well-known equation, $K = ma(u + v)$.

The essential constants of the hydrate theory are, however, quite as simple as those of Arrhenius's theory. For any given solution the chief constants are:—1. The total hydration H , of the solution, which expresses the total number of molecules of water present per molecule of salt.

2. The coefficient of combination β , which expresses the

fraction of the total quantity of water that is actually combined with the salt to form hydrates. 3. The product of these two quantities will give the average composition of the hydrates in solution; this may be termed the "molecular hydration" of the solution, and may be represented by the symbol h . Thus $h = \frac{H}{H_0}$ may be regarded as the fundamental equation of the hydrate theory.

Jones and Getman and Biltz have attempted to determine the molecular hydration of dissolved salts. Assuming that the abnormally great molecular depressions of the freezing-point of salt solutions of moderate concentration were due to a combination of solvent and solute, Jones and Getman were able to compute the amount of solvent water remaining in the solution by comparing the observed molecular depression with that calculated from the coefficient of ionisation of the solution.

The author, after correcting the figures—in which two serious flaws were made—calculated by Jones and Getman, shows that the corrected values point to a regular increase of molecular hydration as the dilution increases, and are, therefore, in accord with the view that ionisation involves an increase, and not a decrease, in the hydration of the solute.

8. The theory may easily be extended to non-aqueous electrolytes in which ionisation may again be attributed to the superior combining power of the ions as compared with the molecules of the dissolved salt.

9. In the case of autoytic salts, which became conductors when fused, it is known that polymerisation is an essential characteristic of these, hence it is only necessary to suppose that the complex molecules of these are associated with the ions. Evidence of the formation of complex ions has recently been obtained in the case of fused salts by Lorenz and Fausti, who have shown that, in fused mixtures of lead chloride with sodium and potassium chlorides, the transport values prove that the lead is present in the form of a complex anion which travels in the opposite direction to the current. Their experiments afford direct evidence of the presence in the fused salt of positive and negative ionic complexes.

Conduction in mixtures of solid oxides, such as the Nernst filament, is doubtless electrolytic in character. Like glass, this filament has the composition of an electrolyte, but behaves as an insulator until the temperature has been raised sufficiently to permit ionic migration to take place. Temperature-conductivity curves for filaments of very various compositions have been plotted by Reynolds, and are very similar in form to those for glass, or for over-cooled, concentrated, aqueous solutions of calcium chloride or sulphuric acid. An even more striking resemblance is to be seen between the family of curves given by Reynolds for the conductivity of mixtures of ZrO_2 and Y_2O_3 at 900° , 1000° , 1100° , 1200° , and 1300° C., and the isothermal conductivity-concentration curves for mixtures of sodium hydroxide and water at 0° , 18° , 50° , and 100° C. The appearance of the two series of curves is such as to warrant the conclusion that the mechanism of conduction is essentially the same in the two cases.

Mr. H. D. LAW pointed out that molecular mobilities were often largely influenced by the undissociated molecules; an ion might wander more quickly through its own molecule than through another. He thought that the experimental evidence on which the hydration was based was as yet somewhat slender.

Dr. C. H. DESCH hoped that Dr. Lowry would develop the theory on the mathematical side. The unsymmetrical pulls, due to electric attractions, on an atom in a solution might be sufficient to cause an interchange of ions, and so explain how conduction occurs in solutions.

Mr. W. R. BOUSFIELD (communicated) showed that the experimental investigation of the relation between hydration and ionisation could be approached along three conveying lines; firstly, on the assumption of a rectilinear relationship between freezing-point depression and concentration; secondly, on the assumption that the amount of contraction per gramme of solute, in aqueous solutions,

is a measure of the combination between solvent and solute; and thirdly, by a consideration of the variations of ionic sizes with temperature and concentration based on the application of Stokes's theorem on the movement of small sphere in a viscous fluid. The results of these three lines of investigation indicated the generalisation, pointed to by Dr. Lowry, that the amount of combination of solvent with solute increased progressively and continuously with increasing dilution. With regard to the conductivity of water, he inclined to the opinion that the H and OH ions were not entirely anhydrous, but were combined with a smaller proportion of water than any of the other ions, and that the conductivity of water depended upon a volatile organic impurity.

Dr. F. G. DONNAN (communicated) drew attention to the work of Werner, who first showed how it was possible to bridge over the gap between the "hydrate" and the "ionisation" theories.

Mr. G. T. BEILBY, referring to the author's views on solid conduction, said that recent observations of his seemed to prove that the impact of electrons (*e.g.*, β -rays) was able to produce electrolysis—ionisation—in solid crystals, such as calc-spar.

PHYSICAL SOCIETY.

Ordinary Meeting, May 26th, 1905.

THE meeting was held at the National Physical Laboratory by invitation of the Director, Dr. Glazebrook. The Laboratory was open to the inspection of Fellows, and the following special demonstrations were shown:—

The Specific Heat of Iron at High Temperatures, by Dr. J. A. HARKER.

A knowledge of the specific heat of iron is important in the determination of high temperatures by calorimetric methods. Dr. Harker has determined the total heat of iron up to temperatures of 900° C. by heating the specimen in an electric furnace, the temperature of which was determined by a resistance thermometer, and dropping the iron into a water calorimeter. A difficulty arises at high temperatures owing to the oxidation of the iron when it comes in contact with the water in the calorimeter, and it is necessary in these circumstances to enclose the specimen by a suitable shield. Quartz tubes were tried, but it was invariably found that they splintered when immersed in the calorimeter. The difficulty was overcome by having in the calorimeter a vertical cylindrical brass tube, filled with magnesia, terminating at its upper end in a hemispherical cup. The iron, in the form of a cylinder the diameter of which was slightly less than that of the tube, was dropped into the magnesia. The extreme flocculence of the powder allows the iron to go straight to the bottom of the tube, and it is thus protected from oxidation. Dr. Harker illustrated by curves some of the peculiarities of the specific heat of iron at high temperatures.

Dr. HARKER also exhibited some New Types of Electric Furnace for the attainment in absence of noxious gases of temperatures between 800° C. and 2200° C.

The conductor conveying the electric current is a tube of solid electrolytes similar in composition to the filament of a Nernst lamp. An essential feature is that, for many purposes the usefulness and life of a furnace constructed in this way may be much increased by adopting a "cascade" system of heating. That is, the energy supplied may be divided, so that only sufficient is put through the tubular conductor to raise its temperature say 1000° C., above its surrounding, the surrounding itself being maintained at 1000° C., thus enabling a temperature of 2000° C. to be attained in the tube without straining it unduly. The regulation of temperature in small furnaces of this type is so perfectly under control that very well defined melting-points may be taken with very small quantities of substance. The thermoelectric method has been used in these

furnaces for determining the melting-point of platinum, the mean result of the experiments giving $1710^{\circ}\text{C.} \pm 5^{\circ}\text{C.}$

Mr. A. CAMPBELL exhibited Apparatus for the Measurement of small Inductances.

The method of measurement is that adopted by Max Wien, and described by him in a paper on "Magnetisation by Alternating Currents" (*Wied. Ann.*, [13], Aug., 1898). It is a modification of Maxwell's method of comparing two self-inductances, the source of voltage being alternating, and the indicating instrument a tuned optical telephone or vibration galvanometer.

In the Optical Department two new optical benches constructed for the Laboratory by Messrs R. and T. Beck were shown by Mr. SELBY.

One of these is specially designed for the rapid testing of spherical and cylindrical lenses, such as are found in oculists' trial cases. The bench consists of two parallel steel bars of circular section, 14 feet long, supported on four cast-iron standards. The carriage carrying the lens-holder is moved along the bench by an endless steel tape which passes over pulleys at the ends of the bench, the movement being produced by rotation of the pulley at the eye end: the focal length of the lens is read on the tape at this end of the bench. The most novel feature in the design is the arrangement provided for rotating the lens-holder from the eye end, for the determination of errors of centring of spherical lenses, and errors in the position of the axis in the case of cylindrical lenses. A triangular tube, which extends along the whole length of the bench, passes through a rotating fitting which projects from the lens-holder carriage. By means of gut belting and a spring pulley, rotation of the triangular tube is transmitted to the lens-holder.

The second bench is designed for the determination of the loss of light by absorption and reflection in telescopes and binoculars. The carriages with the various parts of the apparatus move on rollers along the bench. A parallel beam of light from a collimator passes through the telescope adjusted for infinity, and a lens interposed forms an image of definite size of the aperture of the telescope-objective on the screen of a photometer, where the illumination can be compared with that from a standard source. Comparative measurements can in this way be made; for an absolute measurement the magnifying lens is omitted, and two similar telescopes, or the two halves of a binocular, are set back to back. The light then transmitted is compared with that which passes through an aperture of the same size as the object glasses of the telescopes when the telescopes are removed.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxl., No. 18, May 1, 1905.

Researches on Chemical Combination. — M. Berthelot.—The author's present series of experiments form a continuation of his former research on the influence of the rapid cooling from a very high temperature on chemical combination. He specially concerns himself with the formation of ammonia gas from its constituents—nitrogen and hydrogen. The possibility of this formation by means of a hot and cold tube has been admitted, though hitherto under not well-defined conditions.

Permeability of Quartz Tubes. — M. Berthelot.—The author experiments on the permeability of quartz vessels to hydrogen at various temperatures. He finds that, up to a temperature of about 800° with a quartz wall of about 0.7 m.m. in thickness, the diffusion of the gas is almost

imperceptible. On the contrary, at 1300° the transpiration is very decided, both during experiments on the decomposition of ammonia gas and of hydrogen carbides. His experiments also show that, at a high temperature, oxygen traverses quartz walls more rapidly than nitrogen, whilst hydrogen permeates more than either oxygen or nitrogen. He is now making a new series of experiments on the permeability of glass to gases at temperatures approaching its softening point.

Action of Mercuric Iodide on Sulphuric Acid and Mercury Sulphates. — Alfred Ditte.—When mercuric iodide is heated with mono-hydrated sulphuric acid this iodide turns yellow at 126° . At 200° it begins to sublime, and condenses on the walls of the flask. As the temperature rises iodine vapours are given off, and condense in the neck of the flask. The production of iodine is surprising, as under theoretical conditions the reaction would be $\text{HgI}_2(\text{sol.}) + \text{H}_2\text{SO}_4 = \text{HgO} \cdot \text{SO}_3 + 2\text{HI} - 62.1 \text{ cal.}$; this reaction being strongly endothermic. The author's experiments show, however, that the action of the air causes the production of the iodine.

Preparation of Anhydrous Chlorides of the Rare Earths. — Camille Matignon.—The author prepares large quantities of anhydrous chlorides of the rare earths by taking the following precautions:—The solid material, obtained by evaporation of the hydrochloric solution of the rare earth oxide, is heated in a current of chlorine and hydrochloric acid gas charged with vapours of chloride of sulphur. This evaporation is effected at 130 – 140° , and a substance is produced which contains very little oxychloride, and whose composition is very near the mono-hydrated chlorides to which the author has previously drawn attention. The final molecule of water is rapidly got rid of under these conditions, the residue finally containing no trace of oxychloride. By preparing the chlorides by this method, the author was enabled to examine the properties of the chlorides of lanthanum, neodymium, praseodymium, samarium, and yttrium.

Cæsium Amide. — E. Rengade.—Cæsium-ammonium decomposes spontaneously, but very slowly, into the amide and hydrogen. The formation of the amide is much more rapid if gaseous ammonia acts on the metal at 120° . The amide formed is decomposed by water into ammonia and the hydrated oxide of cæsium, $\text{CsNH}_2 + \text{H}_2\text{O} = \text{CsOH} + \text{NH}_3$. It is very easily soluble in liquid ammonia, and this solution rapidly absorbs oxygen at ordinary temperatures, giving the hydrate and cæsium nitrite with a little nitrate. The author also shows that this oxidation of the ammoniacal solution of the amide is not peculiar to cæsium; it is similarly produced in the case of the amide of potassium. In the case, however, of sodium amide, oxygen is without action in the presence of liquid ammonia; the sodium amide remaining insoluble in liquid ammonia.

New Reagent for the Detection of Potassium. — Eugenio Piñerua Alvarez.—Already inserted.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxviii., No. 5, 1905.

Action of Sulphur on Aniline and Aniline Chlorhydrate. — O. Hinsberg.—On fusing together aniline, aniline chlorhydrate, and sulphur at 170 – 180° , four crystalline substances are formed, viz., diphenylamine, dithioaniline (melting-point 76 – 77°), Merz's thioaniline in which both amino groups are undoubtedly in the para position towards the sulphur, and a thioaniline which melts at 58° . Hofmann, however, under similar conditions obtained as the chief product of the reaction a thioaniline melting at 85.5° , as well as a substance of the formula $\text{C}_8\text{H}_{14}\text{N}_2\text{S}_2$, which has not been further investigated, and some diphenylamine, but the author cannot confirm Hofmann's result. Neither of the two new compounds the author has thus prepared appears to be of a labile nature, readily passing into the other. Merz's thioaniline is exceedingly stable, and the compound of melting-

point 58° is also perfectly stable, being unaltered on boiling with alcoholic potash, concentrated hydrochloric acid, and aniline, and also on treating with iodine. The two thioanilines must evidently be position isomers, Merz's base being the *p-p*-compound, while the compound with melting-point 58° must be the *o-p*-compound.

Phosphoric Acid Esters.—A. Arbusoff.—The preparations obtained by the action of PCl_3 on alcohols are apparently not simple esters of the formula P(OR)_3 , but mixtures of at least two or three substances from which the pure esters can be prepared by fractional distillation under reduced pressure. This method of separating the three series, P(OR)_3 , $\text{P(OR)}_2\text{OH}$, and OP(OR)_3 , is very tedious, and the first series may be most readily isolated by treating the mixture with cuprous chloride, iodide, or bromide, when well defined crystalline compounds are obtained. Two types of these copper compounds exist, containing one molecule of copper haloid combined with one and two molecules of the ester P(OR)_3 respectively.

MEETINGS FOR THE WEEK.

- MONDAY, 5th.**—Royal Institution, 5. General Monthly Meeting. Society of Chemical Industry, 8. "Manufacture and Use of Art Papers," by R. W. Sindall. "Influence of Gelatin Sizing on the Strength of Paper," by Clayton Beadle and Henry P. Stevens.
- TUESDAY, 6th.**—Royal Institution, 5. "Velazquez—The Impressionist," by the Rev. Henry G. Woods, D.D.
- WEDNESDAY, 7th.**—Society of Public Analysts, 8. "Separation of Strychnine and Brucine," by D. L. Howard. "Ammonium Oxalate—its Formula and Stability," by P. V. Dupré. "Notes on some Abnormal Milks from Cleveland and South East Durham," and "A Simple and Convenient Camera for Photo-micrographic Work," by A. C. Wilson. "Composition and Analysis of Milk," by H. Droop Richmond.
- THURSDAY, 8th.**—Royal Institution, 5. (The Tyndall Lectures), "Electromagnetic Waves," by Prof. J. A. Fleming, F.R.S., &c.
- FRIDAY, 9th.**—Royal Institution, 6. "Submarine Navigation," by Sir William H. White, K.C.B., F.R.S.
- SATURDAY, 10th.**—Royal Institution, 3. "Exploration in the Philippines—Among the Head Hunters of North Luzon," by A. Henry Savage Landor.

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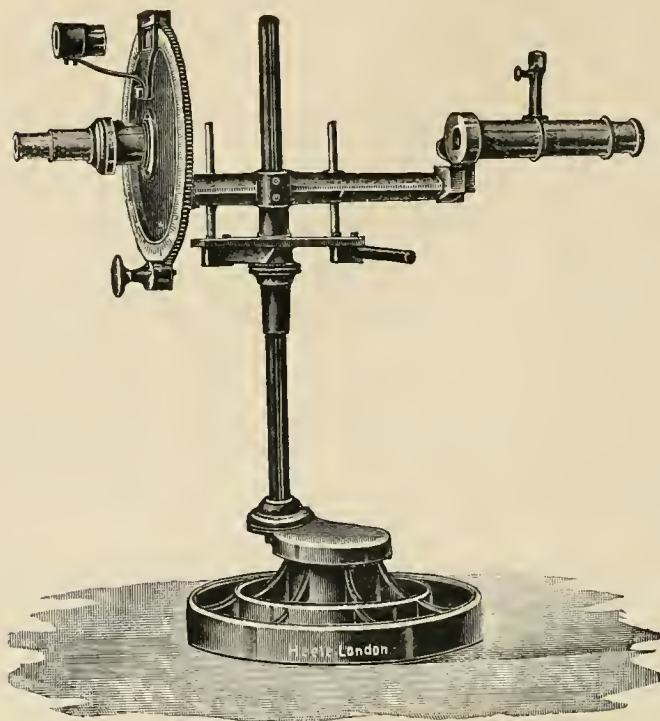
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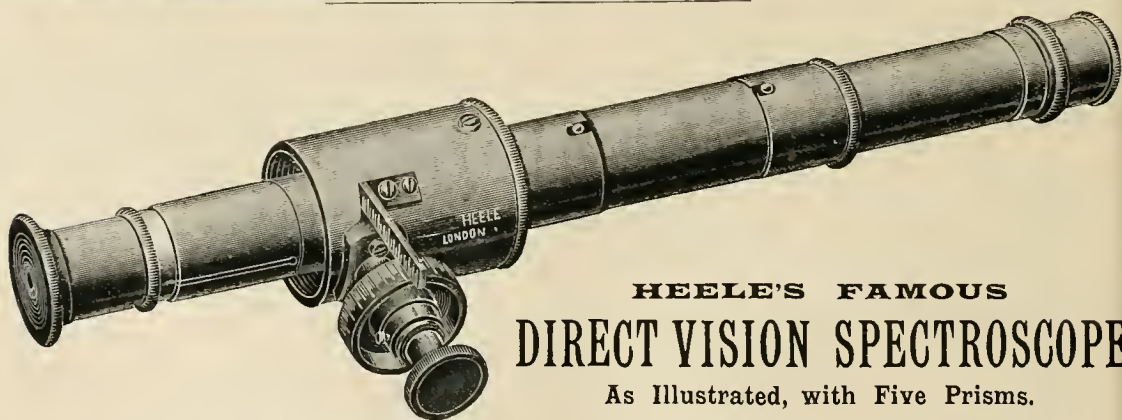
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THE CHEMICAL NEWS.

VOL. XCI., No. 2376.

ON THE CHEMICAL SEPARATION OF THE RADIO-ACTIVE COMPONENTS OF THORIUM COMPOUNDS.

By RICHARD B. MOORE and HERMAN SCHLUNDT.

IN the course of their extended researches on the radio-activity of thorium, Rutherford and Soddy (*Journ. Chem. Soc.*, 1902, lxxxi., 837) discovered a chemical method of separating from thorium compounds a radio-active type of matter—thorium X—which is responsible for the greater part of their activity. The method employed consists in precipitating the thorium as hydroxide from a dilute aqueous solution of the nitrate by the addition of ammonium hydroxide in excess. The filtrate, after evaporation and ignition to expel ammonium salts, yields a very minute residue containing the major part of the activity. Other reagents, such as oxalic acid, di-sodium hydrogen phosphate, &c., Rutherford and Soddy found did not make the separation, the filtrates after evaporation yielding residues which possessed no activity. In fact, ammonium hydroxide was the only reagent tried by Rutherford and Soddy which removed thorium X from thorium compounds.

This communication constitutes a brief preliminary report on several new methods of removing thorium X from the ordinary thorium compounds on the market.

The separations were carried out with aqueous solutions of thorium nitrate by precipitating the thorium completely, evaporating the filtrate, and igniting the residue to decompose or expel the excess of the reagent used. The residue was then tested for radio-activity by the electrical method and the rate of decay determined.

Among the reagents tried, the following remove thorium X from solutions of thorium nitrate:—Pyridine, fumaric acid, aniline, potassium xanthogenate, hydrogen peroxide, ammonium fumarate, benzoic acid, and phenyl hydrazine. In fact the greater proportion of the reagents tried, which precipitated the thorium completely, yielded filtrates whose residues were strongly radio-active. The type of radio-active matter, thorium X, is therefore readily dissolved by a variety of compounds which precipitate thorium.

When the separation is made by means of ammonium hydroxide, Rutherford and Soddy found that the matter causing excited or imparted activity remained in the precipitate. In some of the separations studied by us, it was found that the stage of the imparted activity, which decays to half value in eleven hours, was soluble in excess of the reagent employed, while the one hour stage was precipitated with the thorium. In such cases the initial irregularities of the curves of decay and recovery of the filtrate residue and the precipitate were different from those obtained when the separation is carried out by means of ammonium hydroxide (Rutherford and Soddy, *Journ. Chem. Soc.*, 1902, lxxxi., 840). These initial irregularities are, however, readily explained on the new view recently put forward by Rutherford (*Phil. Trans.*, A, 376), and independently by Miss Slater (*Phil. Mag.*, May, 1905, p. 628), regarding the sequence of the two stages of the imparted activity, viz., that the slow stage is the inactive one and that it precedes the one hour stage, which is the active one.

By applying the two methods of precipitation successively, the matter causing the imparted activity with the slow decay was obtained separate from a thorium nitrate solution. The thorium X was first removed by means of ammonium hydroxide. The precipitate, containing besides the thorium hydroxide, both stages of imparted activity,

was re-dissolved in hot dilute nitric acid, and the excess of acid expelled by gentle heating. After being dissolved in hot water the thorium was again precipitated with fumaric acid (Metzger, *Journ. Am. Chem. Soc.*, 1902, xxiv., 901). The filtrate, after evaporation and ignition, gave a slight residue which has the characteristic curve of decay (Rutherford, "Radio-activity," p. 260), obtained by exposing a negatively charged wire for a short time to the thorium emanation. Conversely, by precipitating the thorium nitrate solution first with fumaric acid and then adding ammonium hydroxide to the filtrate, a very small precipitate was obtained containing the slow stage of the matter causing the imparted activity.

After removing both thorium X and the slow stage of imparted activity, the rapid stage may be obtained in part by re-dissolving the precipitate and subjecting the solution to electrolysis for a short time after the manner of Pegram (*Physical Review*, 1903, xvii., 424) and Von Lerch (*Ann. der Physik.*, 1903, [4], xii., 745), using, however, a high current density and a rotating cathode. The active deposit on the cathode decays to half value in fifty-five minutes, and within a few hours becomes entirely inactive, and remains so. Inactive thorium was not obtained, but precipitates were obtained whose total activity in the course of a month increased to six times their minimum value.

We have jointly undertaken a detailed study of the chemical methods for separating the radio-active types of matter in thorium compounds. Our attention has thus far been given chiefly to the separation by means of pyridine and fumaric acid, a full account of which will appear shortly. Work with specially purified thorium nitrate is now in progress. The samples of the nitrate used in the present experiments were obtained from Eimer and Amend, New York.

University of Missouri, U.S.A.

May, 1905.

ON SOME CONSTITUENTS OF MANCHESTER SOOT.*

By Professor EDMUND KNECHT, Ph.D., F.I.C.

THE coal burnt in Manchester and its immediate surroundings is chiefly what is known as a "fat coal," which, although possessing a high calorific value, is known to yield, especially when used in the household, an abnormally large proportion of smoke and soot. It is to this circumstance that we must ascribe the vitiated condition of the atmosphere in which we exist for the greater part of the year, with its attendant evil effects on the respiratory organs, the desolate appearance of plots of land in the city and its immediate neighbourhood, the dirty condition of all out-of-door objects, the enormous amount of labour involved in keeping the interiors of houses clean, and lastly, to a large extent, the inconvenience experienced by individuals and the trade and commerce of the city caused by such dense black fogs as we experienced last winter.

Having had occasion to examine during February, 1902, some samples of surface snow which had been collected in the centre of the city, and in one of its suburbs, it struck me that it would be of interest if we could obtain some further knowledge of the constituents (more particularly those of organic origin) of the smoky atmosphere we live in, and experiments were undertaken with this end in view, in the carrying out of which I was assisted for a brief period by Mr. Percy Gaunt and by Mr. Cresswell Milnes. Although I am conscious of the fact that the investigation was far from being complete, circumstances at the time did not permit of the further working out of details, and as I do not see my way to enter into the matter again (at all events in the near future), I take the liberty of bringing before you the results which we have so far obtained.

* From *Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, xlix., Part III.

It is popularly supposed that the visible products of the incomplete combustion of coal and other fuel consist merely of finely-divided carbon; and this view is frequently supported in works of a scientific or semi-scientific character. There can be no doubt that this view is to a large extent correct in the sense that these visible products contain finely-divided carbon, but that other solid constituents are met with in not inconsiderable amounts in the soot which is deposited from smoke, has been well known for a long time to the manufacturer of carbon blacks.

The manner in which smoke forms from coal burning in our open fire-grates cannot have escaped the attention of even the most casual observer. It will be quite evident from the voluminous disengagement of gases or vapours that in the first instance dry distillation takes place. Where such disengagement is moderate, the vapours take fire and burn with a bright luminous flame; but if the disengagement becomes violent, the vapours either do not burn at all, or only suffer partial combustion, and their bulk finds its way, mixed with a large excess of air, into the chimney. When the first violent disengagement of gas has ceased, the coal burns quietly with a lurid flame, from which no dry distillation products, but only products of incomplete combustion, result. From these considerations I think we may take it that our smoke and soot consist partly of dry distillation products and partly of the products of incomplete combustion, to which must be added the mineral matter, which is partly volatilised by the heat of the fire, and partly carried away mechanically by the draught.

Our original idea of ascertaining the composition of coal smoke proper presented difficulties which we did not see our way to overcome, so we chose the next best expedient of subjecting ordinary chimney soot to a more exact examination. The first samples examined were taken partly from chimneys in my own house and partly from other chimneys, but were found to vary so much in composition that it was ultimately decided to obtain an average sample from a dealer, and this subsequently served for all our quantitative experiments.

(A large proportion of the household soot collected in Manchester is sold to dealers, who in their turn dispose of it for agricultural or horticultural purposes. I am informed that some is sold locally, but that the bulk goes to Kent, where it is used as a manure for hops. Its effective constituent as a manure consists of salts of ammonia. At the same time, however, it acts as an insecticide, and this property is possibly due to the presence of pyridine and allied bases. At any rate it is certain that its value as a manure cannot depend altogether upon the amount of ammonia it contains, as its price (3s. per cwt.) would be far too high in proportion to the percentage (10–15) of the latter).

In consequence of its constant exposure, while in the chimney, to a current of warm air, this soot may have lost some of its more volatile constituents, and these would in that case have escaped observation. Again, it is quite likely that in one and the same stack the composition of the soot will vary according to the distance from the fire, but this question was not gone into.

The methods employed for separating and isolating the constituents were similar to those which are used in the treatment of coal-tar. The soot was extracted with boiling dilute sulphuric acid, with the object of removing basic constituents; then with caustic soda, to remove acid constituents and phenols; and lastly with benzene, to extract the hydrocarbons. Modifications of this mode of procedure were also tried, for the sake of convenience. Thus, in one series of experiments, the soot was first extracted with benzene, and the extract, after evaporating off the solvent, treated with sulphuric acid and then with caustic soda. In another case the soot was extracted with benzene, and this extract was treated with caustic soda only (previous experience having shown that practically none of the basic constituents were taken out by the

benzene). The benzene extract was separated from the soda lye, and from the black tar which formed a middle layer, and in this case was the only portion further worked on.

Aqueous Extract.—In all the samples of Manchester soot which came under examination, it was found that the aqueous extract showed a strongly acid reaction, due to the presence of free sulphuric acid, which amounted on an average to about one per cent.* The aqueous extract contains practically all the ammonia and pyridine bases. By a tedious process of extraction, I succeeded in isolating from it both ammonium sulphate and ammonium chloride by purely mechanical means.

Sulphuric Acid Extract.—500 grms. soot were boiled for several hours with 4 litres dilute sulphuric acid, filtered, washed, and the united filtrates evaporated down to a quarter of the original bulk. A considerable quantity of a crystalline deposit thus separated, amounting to 9.5 grms. This was found on examination to consist of an impure calcium sulphate. It is noteworthy that the same deposit was obtained with all the Manchester samples worked on as well as with the Prague sample. It might have been taken for granted that the presence of calcium sulphate was due to the action of the sulphuric acid on the mortar in the chimneys, but the occurrence of this substance in surface snow would appear to indicate that the lime had come out of the coal. The filtrate from the calcium sulphate was of a clear light brown colour, and was found on analysis to contain ammonia equivalent to 10.7 per cent ammonium sulphate on the weight of the original soot. This extract was not further examined.

Caustic Soda Extract.—1000 grms. soot were extracted as before with boiling dilute sulphuric acid and washed. The residue was then boiled for three hours with eight litres water and 200 grms. caustic soda. A dark brown liquid resulted, which was filtered off, and the acid constituents precipitated by acidulating with dilute sulphuric acid. The product thus obtained amounted to 109 grms. It was of a rich brown colour, and possessed a strong sooty smell. On heating it neither melts nor volatilises, but simply chars with evolution of but little gas. It resists nitration and sulphonation, and is soluble in boiling sodium carbonate. The solution in caustic soda is not precipitated by carbonic acid. In its general properties the substance (which is nitrogenous) would appear to resemble some of those indefinite brown organic substances which are classed as humic acid.†

A portion of the caustic soda extract, melted in the well known manner with sodium sulphide, yielded a sulphide colour which resembles in its tinctorial properties the best brands of Cachou de Laval, and dyes cotton in absolutely fast shades from a light fawn to a brown black, according to the amount of colour employed.

Benzene Extract.—The residue from the caustic soda extract was dried and then extracted with hot benzene. The solvent assumes a deep brown colour, and the extraction is soon complete. After evaporating off the benzene, a greasy, almost black, residue, was obtained, amounting to 13 per cent by weight of the original soot. It is sticky, and possesses the consistency of butter at the ordinary temperature, but readily softens on warming. When heated, it froths and burns with a smoky flame. For further treatment, the product was gently heated until the frothing had ceased, when it solidified on cooling to a brittle black shining mass. This was then rapidly distilled from a glass retort, and the distillate collected in two portions. The first of these, amounting to 28 grms., formed a clear brown oil; the second, amounting to 6 grms., a light reddish coloured, very thick fluid, which sets at once on cooling.

* A sample of soot which came from a suburb of London (E.) also yielded a strongly acid aqueous extract, whereas a sample which I obtained from Prague (lignite coal) gave an extract which was neutral to litmus paper.

† According to Köhler (*Die Fabrikation des Russes*, p. 13) a brown pigment known as *bistre* was formerly prepared from the soot which separated as a glossy black coating near the fire.

The first distillate, after standing for some time at a low temperature, became semi-solid, owing to the separation of crystals, which were filtered off and purified by re-crystallising several times from boiling absolute alcohol. The substance was thus obtained as a mass of interlaced, beautiful silver-white crystals, which showed a constant melting point of 59.5° . The crystals being soft, their beautiful appearance is spoiled by handling. As the yield only amounted to 0.294 grm., it was not possible to go very deeply into means of identification. The substance dissolved in carbon tetrachloride does not discolourise a dilute solution of bromine in the same solvent. It is slightly soluble in boiling alcohol, but practically insoluble in the cold. Furthermore it appears to resist nitration and sulphonation. The mean of two combustions yielded the following figures:—

	Per cent.
C	84.8
H	14.1
	98.9

From these data it would appear probable that the substance is a saturated hydrocarbon of the paraffin series, and from its melting point and appearance it might be inferred that it is probably identical with the Heptacosane $C_{27}H_{56}$ (m.p. 59.5°) which Schwalb isolated from bees' wax (*Lieb. Ann.*, 235, p. 117).

The filtrate from this characteristic crystalline substance showed a sp. gr. of 1.056 at 15° . It was subjected to distillation in a partial vacuum (80 m.m. pressure). It began to distil at 70° , and the temperature gradually rose to 285° , when it went up suddenly to 305° . At this point the distillate began to thicken, the thermometer slowly rising to 340° , and then suddenly to 400° , when practically all had passed over, and the operation was stopped. The resulting thick brown oil, amounting to 18.5 grms., was soluble in alcohol, ether, benzene, and glacial acetic acid.

The second part of the distillate was not sufficient in amount to allow of a more careful examination. Its solution in benzene and in alcohol shows a characteristic intense green fluorescence. From the alcoholic solution I succeeded in isolating a very small quantity of beautiful sulphur-yellow crystals.

It is evident from the behaviour of the benzene extract in distilling that it consists mainly of hydrocarbons of high boiling points. As these range in the first distillate from 170° to 400° (at 80 m.m.), it would further appear probable that they represent a complex mixture.

Soot after Extraction.—After extracting successively with acid alkali and benzene, the soot, though much darker than before extraction, still showed a brownish black colour, which is possibly due to the considerable amount of ash which it contains (the original sample contained 19 per cent of a red-brown ash). In this condition it is extremely inflammable; in fact, it takes fire spontaneously at a temperature of about 100° , and is then difficult to extinguish. A large plate, containing the extracted soot taken from the drying stove, was seen to contain a little glowing carbon at one point, and this was extinguished. After a short time, however, it began to glow in a different part, and this being also extinguished, another part took fire, and so on, until it was nearly cold.

The following table gives the amounts of constituents estimated directly:—

	Per cent.
Ammonium sulphate	10.7
Mineral matter (ash)	19.6
Acid constituents	10.9
Benzene extract (hydrocarbons)	13.0
Difference (carbon?)	45.8
	100.0

The sample of London soot alluded to above was found to contain considerably less extractive matter than the

Manchester sample. The difference was especially noticeable in the case of the benzene extract, which in the London sample only amounted to 1.3 per cent.

A sample of soot from Prague, for which I am indebted to Dr. F. Rademacher, showed that the products of the incomplete combustion of their lignite coal are of a very different character. The soot, which is of a brown colour, gave an aqueous extract which was neutral to litmus paper. On evaporating down the solution, calcium sulphate separated out in almost colourless crystals. The acid extract contains only traces of ammonia. Of acid constituents soluble in caustic soda I found 2 per cent, while the benzene extract only amounted to 0.2 per cent.

From the brief and incomplete account which I have brought before you, it is at least evident that the composition of Manchester soot is more complicated than is usually imagined. The cause of one of its most characteristic properties, viz., its disagreeable smell, I was unable to trace. It has been ascribed to pyridine bases, but I do not know on what experimental basis this assumption is made. Certain it is that it pervaded all the various products which were isolated, and is even possessed by the re-crystallised, colourless hydrocarbon which was obtained from the benzene extract. To my mind, the smell is more akin to humus or to the peculiar odour which is given off from the earth when a shower of rain falls after a period of dry weather, than to that of pyridine. It would be interesting if one could ascertain what proportion of the solid matter contained in smoke is retained by the walls of the chimney as soot, and what proportion enters the atmosphere. This would of course depend largely on the conditions, such as quality of coal, construction of the hearth or grate, length and width of stack, and to a certain extent whether the chimney had been recently swept or not. In any case, however, I should be inclined to say that in a household fire by far the greater portion of the solid particles enters the atmosphere, and that the accumulated soot consequently only represents a comparatively small proportion of the separated matter. When high winds prevail, the smoke in the city is carried away so rapidly that its presence is not felt, but with a still atmosphere or a gentle air it falls to the ground, where its presence is best revealed by the appearance of snow which has been lying for some days. Though this is blackest in the city itself, its colour shows that deposition takes place for many miles round Manchester, and it cannot but be that this deposition must exert some influence on plant life. With a clayey or sandy soil, which is not manured or limed, there is nothing to neutralise the free sulphuric acid in which our atmosphere has been shown to abound by various observers, and it is to this circumstance mainly that its destructive action on vegetation must be ascribed.

To suggest a remedy would here be out of place, for it would open up the whole question of smoke abatement in dwellings. It is common knowledge that the average household grate is capable of considerable improvement, as far as efficiency is concerned, but with the coal which is available in this district, no material improvement in the atmosphere can be looked for without some legislation in this respect.

Chloro-ferric Colloids.—G. Malfitano.—Sufficiently dilute solutions of ferric chloride, i.e., about a 0.5 per cent solution, gives on hydrolysis very stable colloids. The author investigates these, and finds that the molecules of $Fe_2O_6H_6$, which are formed by hydrolysis, not being capable of remaining dispersed throughout the mass, become separated from the rest, but are retained in the sphere of attraction of the ions Fe or H. Groups are thus formed in varying proportions, which cannot be considered either as molecules or polymers, but may be written as follows:— $Fe_2(nFe_2O_6H_6)Cl_6.H(nFe_2O_6H_6)Cl$. The physical variations correspond with variations in n , differences in the nature of the electrolyte leading to changes more profound in their character.—*Comptes Rendus*, cxl., No. 19.

ON A NEW TYPE OF ELECTRIC FURNACE,
WITH A RE-DETERMINATION OF THE
MELTING-POINT OF PLATINUM.*By J. A. HARKER, D.Sc., Joule Scholar of the Royal Society,
Assistant at the National Physical Laboratory, Teddington.

(Continued from p. 253).

VII. Summary of Results, and Tables giving Details
of Experiments.

TABLE I. gives a summary of the values obtained in sixty-six determinations made on the melting-point of platinum, no observations recorded in the note-book having been arbitrarily rejected.

Three different furnaces were used—a few experiments having been made in one arranged horizontally—and for many of the junctions perfectly independent determinations were made on different days. For the sake of better showing the degree of concordance obtained, the individual observations made with junction T₉, a commercial 10 per cent iridium of medium thickness—the first set taken—are given in Table II. This set were all made on one day, but by three different observers, one of whom had had no previous experience of the method.

VIII. Data regarding the Thermo-junctions.

In Table III. are summarised further data regarding the different junctions, which are here grouped according to their composition.

* A Paper read before the Royal Society, April 13, 1905.

Column I. gives the distinguishing number of the junction.

II. its composition.

III. the diameter of the wires forming the junction.

IV. its formula directly obtained by comparison with standards or at fixed points between 400° C. and 1250° C.

V. the error of the formula at 0° C.

VI. and VII. the sensitiveness or "thermo-electric power" of the junction at 400° C. and 1700° C. respectively.

VIII. percentage of the t^2 term of the E.M.F. at 1700° C. of the whole E.M.F. at the same temperature.

IX. mean value of the E.M.F. in microvolts given by the junction at the melting-point of platinum.

X. number of experiments made.

XI. mean value given by the junction for the melting-point of platinum in degrees Centigrade.

Junction N. P. L. 3 was part of the stock of 10 per cent platinum-rhodium alloy obtained from Heraeus in 1901. Full particulars regarding junctions N. P. L. 1, 2, and 3 made of this wire are given in the author's paper on high temperature standards previously alluded to. Some of the observations in the second set included under this heading were made with junction N. P. L. 2, the actual wire used

TABLE I.—Summary of Determinations of the Melting-point of Platinum.

Junction.	Date.	Observers.	No. of experiments.	Highest value found.	Lowest value found.	Mean.
T ₉	1904— September 16 ..	J. A. H. W. H. H. C. H. C.	7	1713	1709	1711
M ₉	September 16 ..	J. A. H.	4	1709	1707	1708
N. P. L. 3	September 20 .. October 13	R. T. G. J. A. H.	9	1714	1709	1712
T ₁₄	October 25 1905— January 16 January 28	J. A. H.	14	1707	1703	1705
T ₁₅	1904— October 25 October 27 1905— February 6	J. A. H.	10	1712	1703	1707
M ₄	January 16	H. C. H. C. J. A. H.	3	1705	1702	1704
M ₅	January 16	H. C. H. C. J. A. H.	3	1693	1691	1692
T ₂₀	January 28 January 31	J. A. H.	13	1698	1694	1696
T ₂₁	January 31	J. A. H.	3	1713	1711	1712

TABLE II.—Observations on Melting-point of Platinum with Junction T₉.
(Commercially Pure 10 per Cent Iridium from F., M., and Co.).

No.	Date.	Observer.	Value found.	Mean of group.
1.	September 16, 1904	J. A. H.	1709	—
2.	" "	J. A. H.	1712	—
3.	" "	J. A. H.	1713	—
4.	" "	W. H.	1711	1711
5.	" "	J. A. H.	1709	—
6.	" "	J. A. H.	1712	—
7.	" "	H. C. H. C.	1713	—

TABLE III.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
No. of junction.	Composition of junction.	Diameter of wires in m.m.	Formula for E.M.F. of junction from 400° C. upwards.	° Error of formula at 0° C.	$\frac{dE}{dT}$ at 400° C.	$\frac{dE}{dT}$ at 1700° C.	$\frac{1}{2}$ term $\times \frac{100}{\text{Whole E.M.F.}}$ at 1700° C. Per cent.	Mean value of microvolts at the melting-point of platinum.	Number of experiments.	Mean value of melting-point of platinum in degrees C.
<i>Pure Rhodium Alloys—</i>										
N. P. L. 2 and 3	German rhodium, 10 per cent alloy from Heraeus, 1901	0.62	$-304 + 8.165t + 0.001663t^2$	-37	9.49	13.82	+26	18580	9	1712
T ₁₅	Purest English rhodium, 10 per cent alloy from Johnson, Matthey, and Co., 1904	0.51	$-250 + 7.953t + 0.001842t^2$	-31	9.43	14.21	+29	18693	10	1707
<i>Commercial Rhodium Alloys—</i>										
M ₄	Commercial 10 per cent rhodium from J., M., and Co., 1903	0.48	$-692 + 11.55t + 0.001245t^2$	-60	12.55	15.78	+16	22590	3	1704
T ₂₀	Ditto, a second sample, formerly called T ₆	0.31	$-446 + 11.697t + 0.001416t^2$	-38	12.81	16.51	+17	23415	13	1696
<i>Pure Iridium Alloy—</i>										
T ₁₄	Purest English iridium alloy, drawn from "étalon" wire, J., M., and Co., 1904	0.54	$-409 + 15.7635t + 0.0007339t^2$	-26	16.35	18.25	+7	28581	13	1705
<i>Commercial Iridium Alloys—</i>										
T ₉	10 per cent commercial iridium, J., M., and Co., 1904	0.33	$-442 + 15.6957t + 0.0007349t^2$	-28	16.28	18.19	+7	28532	7	1711
M ₉	Ditto, another sample, 1904	0.50	$-544 + 15.2403t + 0.001749t^2$	-36	16.64	21.18	+17	30600	4	1708
M ₅	Ditto, another sample, 1903	0.33	$-781 + 15.5043t + 0.001186t^2$	-50	16.46	19.52	+12	28840	3	1692
<i>Rhodio-platinum against Iridio-platinum—</i>										
T ₂₁	Iridium alloy of same sample as T ₉ against rhodium alloy of same sample as T ₂₀	0.33 and 0.31	$+4 + 4.0259t - 0.0006809t^2$	+1	3.40	1.8	-40	4905	3	1712

in the direct gas-thermometer comparisons. The three wires coincide to within the limits of accuracy attainable.

T₁₅ is a sample of extremely carefully prepared wire from Messrs. Johnson, Matthey, and Co., made under the personal direction of Mr. George Matthey, F.R.S., to whose kindness the laboratory is indebted for the care spent on the preparation and analysis of a number of specimens of these platinum alloys. Analysis revealed no trace of any other metal present but platinum and rhodium, the figures obtained for these elements being Pt = 89.9, Rh = 8.98, both being directly determined.

(To be continued).

THE ATOMIC WEIGHT OF CHLORINE.*

AN ATTEMPT TO DETERMINE THE EQUIVALENT OF CHLORINE BY DIRECT BURNING WITH HYDROGEN.

By HAROLD B. DIXON, M.A., F.R.S.

(late Fellow of Balliol College, Oxford), Professor of Chemistry, and

E. C. EDGAR, B.Sc., Dalton Scholar of the University of Manchester.

ALTHOUGH the atomic weight of chlorine has been determined by Stas and other chemists with extraordinary care, nevertheless owing to the very indirect methods hitherto used in making the comparison between chlorine and hydrogen, it is possible that a constant error may occur in some link of the long chain of connecting ratios. To join up the open ends of the chain by a direct comparison between chlorine and hydrogen, if it could be done with reasonable accuracy, would serve not only to detect any such systematic error, but would permit the accidental errors to be distributed and prevent their accumulation at the unconnected end. According to Professor F. W. Clarke the accumulated "probable error" in his re-calculated

* Abstract of a Paper read before the Royal Society, May 18, 1905.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 5th inst., His Grace The Duke of Northumberland, K.G., F.R.S., President, in the Chair. Mr. E. Hurry Fenwick, F.R.C.S., and Mr. Oswald Lewis were elected Members. The Special Thanks of the Members were returned to Mr. L. F. Everest for his Present of a Portrait of Colonel Sir George Everest, C.B., F.R.S.

value for chlorine amounts to ± 0.0048 ; the probable error of the mean of our nine determinations is less than ± 0.002 .

It was at the suggestion of Professor E. W. Morley, of Cleveland, U.S.A., that we have attempted this direct comparison by determining the weight of hydrogen which burns in a known weight of chlorine.

Our method was briefly as follows:—

Chlorine prepared by the electrolysis of fused silver chloride (with purified carbon poles in a Jena glass vessel) was condensed and weighed as a liquid in a sealed glass bulb. This was attached to a vacuum combustion globe, and the chlorine allowed to evaporate slowly into the globe. The hydrogen prepared by the electrolysis of barium hydrate solution was dried and then absorbed by palladium in a weighed vessel. The palladium, on being warmed, gave off the hydrogen, which was ignited by a spark, and burnt at a jet in the combustion globe previously filled with chlorine. The gases were regulated so as to maintain the hydrogen flame until nearly all the chlorine had been combined; then the palladium was allowed to cool, and the hydrogen was turned off just before the flame died out. The hydrogen chloride, as it was formed in the flame, was dissolved by water standing in the globe which was kept cool by ice. A little hydrogen chloride was formed by the action of the water-vapour on the chlorine in the flame, a corresponding amount of oxygen being liberated. This oxygen was determined in the analysis of the residual gases, which contained, besides traces of air, the small quantity of hydrogen which filled the capillary tube between the tap and the jet when the flame was extinguished, and any that might escape unburnt from the flame. The chlorine remaining unburnt in the globe was about 2 per cent of that burnt. This unburnt chlorine, as gas and in solution, was determined by breaking thin glass bulbs containing potassium iodide. The residual gases having been pumped out (and any iodine vapour caught by a wash-bottle), the liberated iodine was determined by standard thiosulphate in an atmosphere of carbon dioxide. In the calculation of the unburnt chlorine the atomic weight of chlorine was assumed to be 35.195, and the atomic weight of iodine 126.015.

In each experiment we burnt between 11 and 13 litres of each gas.

The balance, by Oertling, was fixed on a stone pedestal in an underground cellar. The vibrations of the pointer were read by a telescope, Gauss' method of reversals being used. The chlorine and hydrogen bulbs were counterpoised on the balance by bulbs of the same glass and of nearly the same displacement, and the small weights employed in the weighings were reduced to a vacuum standard.

The following were the corrected weights of hydrogen and of chlorine burnt in the several experiments:—

	Hydrogen burnt, in grms.	Chlorine burnt, in grms.	Chlorine combined with unit weight of hydrogen.
1.	0.9993	35.1666	35.191
2.	1.0218	35.9621	35.195
3.	0.9960	35.0662	35.207
4.	1.0243	36.0403	35.185
5.	1.0060	35.4144	35.203
6.	0.9887	34.8005	35.198
7.	1.0159	35.7639	35.204
8.	1.1134	39.1736	35.184
9.	1.0132	35.6527	35.188
Mean . . .			35.195 $\pm$ 0.0019

In the whole of these nine experiments 9.1786 grms. of hydrogen combined with 323.0403 grms. of chlorine, hence the equivalent weight of chlorine, calculated in mass, is 35.195.

The number we have obtained for the atomic weight of chlorine is appreciably higher than that calculated by F. W. Clarke from the previous determinations, and is slightly higher than Stas's value:—

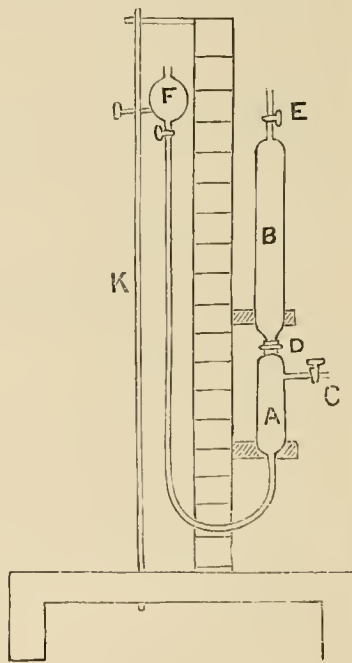
Clarke's calculation.	Stas.	Dixon and Edgar.	H = 1 O = 16
35.179	35.189	35.195	
35.447	35.457	35.463	

Since our experiments were completed we have heard that Professor T. W. Richards is engaged on a revision of Stas's work on the composition of silver chloride. G. P. Baxter quotes the value 35.467 as being obtained by Richards and Wells for the atomic weight of chlorine—a number slightly higher than ours.

A NEW EUDIOMETER.*

By J. WILSON.

THE accompanying drawing is a diagrammatic sketch of an instrument specially adapted for the demonstration of the law of volume combination of gases. It may also be used for proving Boyle's and Charles's laws.



A and B are glass tubes of similar bore, connected by stopcock D. A is provided with side tube and stopcock C, and is also connected by a piece of rubber pressure tubing of small bore with mercury cup, F. B is fitted at upper extremity with stopcock E, and is also provided with wires for sparking gases. A is graduated from D downwards, and B from E downwards.

The apparatus is fitted to a wooden stand, the upright centre piece carrying a metre rule graduated in inches as well as centimetres. Mercury cup F is capable of vertical motion up and down iron bar K.

B is supplied with a steam jacket, which is not shown in diagram.

The apparatus is filled with mercury in the same way as an ordinary Boyle's instrument, care being taken to fill side-tube C.

After filling, D and E are closed. F is brought below level of C, which is opened after being connected with gas supply. Gas is then drawn into A. Connection with gas supply is then broken, and gas in A reduced, at atmospheric

* Patent 10937.

pressure, to volume required, and c then closed. D is now opened, and a little mercury drawn from B into A by lowering F. The gas is transferred from A to B by alternately raising and lowering F. When the gas has been transferred to B it is brought to atmospheric pressure, and D closed. The gas remaining in side-tube C is now driven out. The required volume of the second gas is drawn into A, measured, and then transferred to D in exactly the same way as was the first gas. D is then closed, and the gas driven out of side-tube C, when D is re-opened.

To fill with mercury, to measure the gases, and to bring them together in B do not occupy more than seven minutes.

The sparking of a mixture of hydrogen and oxygen may be performed at a pressure so much below atmospheric pressure that the product may be kept in the form of steam at a temperature considerably below 100° C. Steam may therefore be used as the heating substance.

As the gases are measured accurately before being brought into contact, the instrument is specially adapted for the demonstration of the volume reaction of such gases as hydrochloric acid and ammonia, of chlorine and sulphuretted hydrogen, gases which react on contact.

For the demonstration of Boyle's law and Charles's law gas is admitted into B. Variations in pressure ranging from 300 to over 1200 m.m. are possible.

The instrument is easily cleaned for solvents, may be admitted into A and B in the manner described for gases.

A B is the only expensive portion liable to breakage, and this may be repaired or easily replaced.

The glass parts may be easily removed and replaced, and are therefore readily stowed away when not required for use.

The following table gives, firstly, the spectro-chemical molecular functions of ethyl acetoacetate when dissolved in water, methyl alcohol, or chloroform; secondly, the constants of the homogeneous undissolved ester, and finally those of the ester dissolved in ethyl-alcoholic sodium ethoxide.

Ethyl acetoacetate.	Percentage of ester dissolved.	$\left(\frac{n^2-1}{n^2+2}\right) \frac{P}{d} = M.$		
		$M_1.$	$M_2.$	$M_1 - M_2.$
Dissolved in water .	6.960 8.895	31.61 31.66	31.76 31.82	0.77 0.79
Dissolved in methyl alcohol ..	30.20 56.68	31.87 31.83	32.05 31.98	0.89 0.86
Dissolved in chloroform ..	22.50 44.61	31.93 31.89	32.11 32.05	0.90 0.88
Homogeneous ..	100.0	31.80	31.96	0.87
Dissolved in 12.68 per cent sodium ethoxide ..	19.29	35.38	35.77	2.45

The table indicates, moreover, that the functions of the dissolved ethyl acetoacetate obtained from all solutions in neutral media are practically identical (compare *Ber.*, 1905, xxxviii., 1868).

DISCUSSION.

Mr. Baly asked Prof. Brühl whether he had investigated the compounds under the influence of ultra-violet light. According to experiments on the ultra-violet absorption spectra by Dr. Desch and himself, it appeared that the metallic derivatives in alkaline or neutral solvents are equilibrium mixtures of the two tautomeric forms. It seems probable from these and some later results that the more stable condition of the metallic derivatives is the enolic form, and that under the influence of the ultra-violet light some of the ketonic modification is formed, and an equilibrium between the two forms is set up.

Prof. Brühl, in reply to Mr. Baly, said that he had not investigated aqueous solutions of the sodium derivative of ethyl acetoacetate, but had only examined the substance dissolved in the alcohols. Aqueous solutions are partly hydrolysed, and must therefore contain both the free ketonic ethyl acetoacetate and the enolised sodium derivative. On the other hand, solutions of this derivative in the anhydrous alcohols are not at all hydrolysed, and they contain only a single form, namely, the enolic one.

He also pointed out that Mr. Baly worked in very dilute solutions, and under these conditions the chemical relations would differ from those obtaining in the concentrated solutions used by himself and Schröder.

It is also possible that the very energetic ultra-violet light used by Mr. Baly exerts some action on the solutions of substances capable of being tautomerised.

*89. "The Chlorination of Methyl Derivatives of Pyridine. Part I. 2-Methylpyridine." By WILLIAM JAMES SELL.

When 2-methylpyridine is subjected to the action of a current of chlorine, the molecule for the most part breaks down, and a tarry mass is produced, a similar result being obtained on heating the methylpyridine with phosphorus pentachloride. In these circumstances, recourse was had to the process found successful in the case of pyridine, namely, the chlorination of the hydrochloride saturated with hydrochloric acid. The only solid substance as yet produced as the direct result of chlorination separates as a white crystalline powder having the formula $C_6H_7Cl_2N$. This compound is resolved by gently heating with 80 per cent sulphuric acid into a trichloropicolinic acid, which, on heating with glycerol, gives a trichloropyridine (m. p. 72—73°). Since this trichloropicolinic acid is convertible through its amide by the Hofmann reaction into a trichloroaminopyridine identical with the substance which has been shown (*Trans.*, 1899, lxxv., 980; 1900, lxxvii., 771) to have the constitution represented by the formula—

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, May 17th, 1905.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

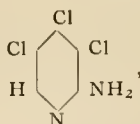
MESSRS. D. L. Chapman and A. E. Bellars were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Edward Williams Bealey, B.A., 55, Belsize Park Gardens, Hampstead, N.W.; William James Bees, B.Sc., 43, Ash Grove, Hyde Park, Leeds; William Robert Bousfield, M.A., K.C., St. Swithin's, Hendon; William Beverly Cowie, 26, East Claremont Street, Edinburgh; William Walpole Day, B.Sc., Eilerslie, Harrogate; Herbert Henstock, B.Sc., Feldeggstrasse, 33, Zürich V, Switzerland; William John Jarrard, B.Sc., 41, Whitting-stall Road, Fulham, S.W.; Arthur Walter Mason, B.Sc., 6, Northumberland Place, North Shields; Frederick Wilson Montrose Ross, 21, Soho Square, W.; James Steger, B.Sc., 111, Chesterfield Road, Bristol; William Bradshaw Tuck, University College, Gower Street, W.C.; John William White, 9, Hampden Place, Halifax, Yorks; William James Wren, 271, Park Road, Oldham.

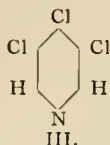
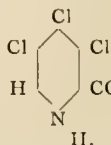
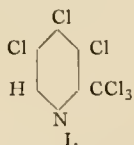
Of the following papers, those marked * were read:—

*88. "The Desmotropic Form of Substances of the Ethyl Acetoacetate Type in the Homogeneous State and Dissolved in Neutral Media." By JULIUS WILHELM BRÜHL and HEINRICH SCHRÖDER.

The authors claim to have established by strict proof that both the primary ethyl acetoacetates and their secondary and tertiary alkyl substitution products, and also the camphorcarboxylic esters and their alkyl derivatives, although liquid, display a pure uniform ketonic structure, and contain no traces of tautomeric enolic structures, which can be demonstrated by experiment.



it is clear that the three foregoing substances may be thus represented:—



DISCUSSION.

Sir WILLIAM RAMSAY asked whether Mr. Sell had investigated a compound obtained by the action of chlorine on picoline, having a smell of bleaching-powder.

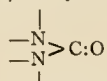
Mr. SELL, in reply, said he had often noticed the substance referred to, but had hitherto found no opportunity of making more than a cursory examination of it. This product is not noticed during the chlorination of picoline hydrochloride, but only when the free base is used.

*90. "The Absorption Spectra of Uric Acid, Murexide, and the Ureides in relation to Colour, and their Chemical Structure." By WALTER NOEL HARTLEY.

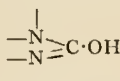
The author refers to a former paper (*Trans.*, 1887, li., 153) of which this is a continuation. He found it necessary to examine the chemical constitution of murexide, and had made considerable progress in this direction, when work on similar lines was published almost simultaneously by Piloty (Abstr., 1904, i., 820), Mohlau (*Ibid.*, p. 654), and Max Slimmer and Stieglitz (*Ibid.*, p. 634).

Murexide was prepared from two sources, namely, alloxantin and alloxan, by boiling with alcoholic ammonia for half-an-hour. Two intermediate products were obtained, the one being colourless with a rich blue fluorescence and a strong absorption band in the ultra-violet, the other a reddish yellow substance which appears to be purpuric acid, the absorption spectra of which were photographed. The ureides, diureides, and some oxypurin derivatives were spectrographically examined. They are divided into two groups, those which show an absorption band and those which do not.

The former are those oximino-ketones with no ethylenic linking associated with the carbonyl groups. On the other hand, those which have one or more such linkings do show bands; other substances, such as alloxantin and dialuric acid, are capable of undergoing a change under the action of water, and these exhibit a band, that of dialuric acid, being identical with that of alloxantin. Others apparently occur in isodynamic forms, the change being rendered evident by the development of a band in a solution which at first shows none. Theobromine and caffeine are examples. Whether the substance shows an absorption band or not is apparently determined by the 8th position in the purin ring being occupied by O, OR (where R is an alkyl or monad metal), or by H.



2 : 6 : 8-Oxypurin
Show spectra with a band.



2 : 6-Oxypurin



6-Oxypurin
Shows no band.

*91. "Observations on Chemical Structure and Physical Properties Associated with the Theory of Colour." By WALTER NOEL HARTLEY.

Owing to certain peculiarities in the absorption spectra of the ureides, the author collates a number of observations on the structure of chromogenic compounds, together with various views regarding the origin of colour in dyes and other substances. Selecting that feature which is common to them all, he seeks to apply it to an explanation of the

absorption phenomena generally observed in the aromatic hydrocarbons and their derivatives. The main feature in a coloured substance is the occurrence in two parts of the molecule of ethylenic and benzenoid groupings, and of ketonic groupings. The ethylenic and ketonic groupings in a molecule are precisely those admitting of a keto-enolic isodynamic change, which, in accordance with the view of Baly and Desch (*Trans.*, 1904, lxxxv., 1029), is the cause of selective absorption. According to J. Schmiiedlin (*Comptes Rendus*, 1904, cxxxix., 872), the two parts of the molecule of a dye must consist of one endothermic and the other exothermic, the former being chromophoric, the latter an auxochrome. It is pointed out that benzenoid and ethylenic groupings are endothermic, whilst a carbonyl group is exothermic; and also that whilst azobenzene is a yellow chromogen, benzene is also a chromogen, but its colour is in the ultra-violet. The explanation based on the change from a double linking (ketonic) to a single linking (enolic) should, if sound, be capable of explaining the occurrence of six bands in the spectrum of benzene, four in that of naphthalene, and four in that of anthracene.

It is shown how this is possible from Kekulé's formula for benzene, and how this formula may be reconciled with the centric formula.

*92. "Further Studies on Dihydroxymaleic Acid." By HENRY JOHN HORSTMANN FENTON.

The mode of formation, properties, constitution, and relationships of dihydroxymaleic acid have been discussed in several previous communications (*Trans.*, 1894, lxxv., 899; 1895, lxxvii., 48 and 774; 1896, lxxix., 546; 1897, lxxi., 375; 1902, lxxxii., 426; *Proc.*, 1898, xiv., 119; *Proc. Camb. Phil. Soc.*, 1901, xi., 109; 1902, xi., 358, &c.), and the present paper gives an account of some of the principal investigations which have since been carried out in connection with this subject.

Results of considerable interest have been obtained from a study of the condensation of the acid with ammonia, and the behaviour of the acid and its esters towards various hydrazines. Further observations have been made on the conditions of formation of glycollic aldehyde and of mesoxalic semi-aldehyde, and the properties of the latter substance have also been further examined.

*93. "The Influence of Light on Diazo-reactions." (Preliminary Notice). By KENNEDY JOSEPH PREVITÉ ORTON and JOSEPH EDWARD COATES, and (in part) FRANCES BURDETT.

Although it has long been realised that certain diazo-compounds are sufficiently sensitive to light to render a "diazo-type" photographic process practicable (Feer, D.R.-P. 53455; Green, Cross, and Bevan, D.R.-P. 56606, *Ber.*, 1890, xxiii., 3131, and *Journ. Soc. Chem. Ind.*, 1890, ix., 1001; and Ruff and Stein, *Ber.*, 1901, xxxiv., 1668), the precise reactions involved do not appear to have been fully investigated. The experiments appear to have been carried out exclusively with solid diazo-compounds. Green, Cross, and Bevan (*loc. cit.*, and *Ber.*, 1901, xxxiv., 2495) state that the primary action of light is to effect a decomposition into phenols and nitrogen.

In the case of the highly substituted diazobenzenes, which are quite stable at the ordinary temperature, the effect of light as an accelerator of certain reactions can be easily studied. The reactions are well illustrated in the remarkable behaviour of *s*-tribromodiazobenzene. On boiling aqueous or acid solutions of *s*-tribromobenzene-diazonium salts, no *s*-tribromophenol is formed (Silberstein, *Journ. Prakt. Chem.*, 1883, [ii.], xxvii., 113; Hantzsch, *Ber.*, 1900, xxxiii., 2517). It has been shown, on the contrary (Orton, *Trans.*, 1902, lxxxiii., 802), that the chief reaction is the elimination of bromine and the formation of dibromoquinonediazide. When aqueous solutions of the diazonium salts are exposed to sunlight, a rapid decomposition into *s*-tribromophenol and nitrogen occurs. The addition of acid has no retarding effect on the rate of the decomposition, but rather increases the yield of *s*-tribromophenol. In the absence of excess of acid, a secondary re-

action, the elimination of bromine and the formation of quinonediazide, becomes noticeable (compare Orton, *loc. cit.*).

The corresponding *s*-tribromobenzenediazotates, on the other hand, are entirely unaffected by sunlight.

Not only are the solutions in water very sensitive to light, but also the solutions in methyl and ethyl alcohols and acetic acid are similarly easily decomposed. *s*-Tri-bromobenzenediazonium salts are remarkable in that their solutions in methyl and ethyl alcohols and in acetic acid yield, on boiling, only *s*-tribromobenzene, and no *s*-tribromoanisole, *s*-tribromophenetole, or *s*-tribromophenyl acetate respectively. In the decompositions effected by sunlight, on the other hand, the main product of the reaction is the methyl or ethyl ether, the anisole, $C_6H_2Br_3 \cdot OMe$, and the phenetole, $C_6H_2Br_3 \cdot OEt$, when methyl or ethyl alcohol are the solvents. The solution in acetic acid yields *s*-tribromophenyl acetate, $C_6H_2Br_3 \cdot OAc$. That the light has a specific accelerating influence on these particular decompositions, is shown by the fact that a solution of the diazonium sulphate in 90 per cent alcohol, which slowly decomposes at the ordinary temperature, yields only *s*-tribromobenzene in the absence of light, but a large proportion of the phenetole when exposed to sunlight. A solution of potassium *s*-tribromobenzenediazotate in methyl alcohol is unaffected by light. The presence of acids and of water in the alcoholic solution has a marked effect on the course of the reaction.

A number of diazonium salts and diazotates have been investigated, similar effects being observed in each case. Solutions of diazonium salts have been kept for many weeks (ten) in the dark without the evolution of a measurable volume of nitrogen; on exposure to sunlight, a rapid change into the corresponding phenol ensues. An interesting example is found in the case of 5-bromo-*m*-xylene-4-diazonium hydrogen sulphate, which is quite stable in aqueous solution at the ordinary temperature so long as light is excluded, but decomposes rapidly either on exposure to light or on heating into the corresponding xenol.

The results lead the authors to conclude that the conversion of diazo-compounds into phenols, ethers, and phenylacetates is a reaction characteristic of the diazonium ion.

DISCUSSION.

Dr. CAIN congratulated Professor Orton on having discovered a method of obtaining certain phenols from the corresponding diazo-salts, which in many cases did not undergo the usual decomposition on boiling with either dilute or strong acids. He took exception, however, to Dr. Orton's statement that the diazo-salt from *s*-tribromo-aniline yielded no phenol when boiled with acids, for although several observers had also recorded their failures to detect any tribromophenyl, he had, by adopting the method described in D.R.-P. 95339, which consisted in dropping the diazo-solution into a boiling mixture of sodium sulphate and dilute sulphuric acid, succeeded in obtaining a small yield (2 per cent) of tribromophenol. He had also noticed that a solution of benzenediazonium chloride on exposure to sunlight deposited a thick, brownish yellow precipitate in a very short time, whilst another portion of the same solution kept in the dark remained perfectly clear.

Prof. ORTON, in reply, said that they had failed to obtain *s*-tribromophenol by Heinichen's method (*Annalen*, 1889, ccliii., 281), namely, by heating with 63 per cent sulphuric acid (b. p. 150°), but they had not tried heating in a concentrated solution of sodium sulphate.

*94. "Behaviour of Solutions of Propyl Alcohol towards Semi-permeable Membranes." By ALEXANDER FINDLAY and FREDERICK CHARLES SHORT.

Some years ago, S. U. Pickering stated (*Ber.*, 1891, xxiv., 3639) that when a porous pot containing a 57 per cent aqueous solution of propyl alcohol was immersed in either pure water or pure propyl alcohol, the water or the alcohol passed inwards to the solution. Pickering, therefore,

ascribed osmotic pressure to the permeability of the membrane for either of the pure components and its impermeability for the hydrate formed in the solution.

The authors have sought, with the use both of porous pots and of copper ferrocyanide membranes, to repeat Pickering's experiments, but they have in no case obtained any indication confirmatory of this observer's results. When simple porous pots were used, the level of the liquid in the manometer tube attached to the porous pot fell in each case, no matter whether the surrounding liquid was water or propyl alcohol. When a copper ferrocyanide membrane was employed, a rise of liquid in the manometer tube was obtained when the pot was surrounded by water, but a fall occurred when the pot was placed in propyl alcohol.

It is conceivable that the behaviour observed by Pickering might be due to differences in the velocity of diffusion of the pure liquids and the solution, but in this case the rise of liquid obtained could only have been temporary, and the experiment would then lose all its significance for the problem of solution.

DISCUSSION.

Mr. PICKERING stated that he could give no further details of his experiment than those which had already been published. There appeared to be no doubt as to the fact observed by him, for the observation was repeated several times. The porous pot used had no semi-permeable diaphragm, but it was only in the case of comparatively impervious pots that the phenomena were apparent; if the pot was too porous, the excess of pressure was not maintained. The result might have been due to ordinary diffusion, but that would not invalidate the explanation given of it.

Dr. FINDLAY, in reply, said that it would appear that the rise of liquid which Professor Pickering had observed in the manometer was only a temporary one, and that, consequently, the explanation which the authors offered of the discrepancy between the two results is the correct one.

*95. "The Thermal Decomposition of Formaldehyde and Acetaldehyde." By WILLIAM ARTHUR BONE and HENRY LEWELLYN SMITH.

The authors show that at all temperatures between 400° and 1125° formaldehyde rapidly decomposes, without any separation of carbon, in accordance with the equation $CH_2O = CO + H_2$, and that the decomposition is not, to any appreciable extent, reversible. At high pressures (concentrations), the simple decomposition may be masked by more complex changes.

At 400°, acetaldehyde decomposes without any separation of the carbon or liberation of hydrogen, in accordance with the equation $CH_3 \cdot CHO = CH_4 + CO$, but at 600° and higher temperatures carbon and hydrogen appear among the products. The effect of a hot surface of porous porcelain, at 450–500°, on the undiluted aldehyde vapour, in absence of oxygen, is to induce the "aldol condensation" with formation of crotonaldehyde and steam.

*96. "The Synthesis of Formaldehyde." By DAVID LEONARD CHAPMAN and ALFRED HOLT, jun.

The authors have succeeded in synthesising formaldehyde by maintaining a platinum wire at a high temperature in the following mixtures:—(a) Carbon monoxide and hydrogen; (b) carbon monoxide, hydrogen, and steam; (c) carbon monoxide and steam; (d) carbon dioxide and hydrogen. All attempts to obtain formaldehyde in appreciable quantities by passing the same gaseous mixtures through heated tubes at temperatures below 500° were unsuccessful.

*97. "Oxymymeric Perchlorates and the Action of Alcohol on Mercury Perchlorates." By MASUMI CHIKASHIGE.

Three new oxymymeric perchlorates are described, making four altogether, with that previously described (*Proc.*, 1895, xi., 164):—(1) Hydrated oxymymeric perchlorate, $OHg_3(ClO_4)_4 \cdot 12H_2O$, crystallising from its cold aqueous solution and decomposing in its boiling solution; (2) the same salt, that is, $\frac{1}{2}$ -basic oxymymeric perchlorate,

rendered anhydrous by boiling alcohol, and thereby greatly altered in stability; (3 and 4) two isomeric $\frac{1}{2}$ -basic oxy-mercuric perchlorates, $O_2Hg_3(ClO_4)_4$, differing greatly from each other, although both are anhydrous. The α -salt, described in the previous paper, is non-explosive, whereas the β -salt, obtained by heating the $\frac{1}{2}$ -basic salt in boiling alcohol, is a powerfully detonating substance.

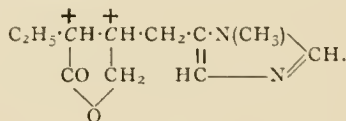
Mercuric perchlorate interacts with boiling alcohol to form mercurous perchlorate, perchloric acid, and aldehyde. The $\frac{1}{2}$ -basic salt is partly reduced to mercurous salt by boiling with alcohol, and partly decomposes into perchloric acid and the β - $\frac{1}{2}$ -basic oxymercuric salt (insoluble in acids). No reduction of perchloric acid occurs, and no trace of chloride is formed.

98. "The Constitution of Pilocarpine. Part IV. Conversion of *isopilocarpine* into *pilocarpine*." By HOOPER ALBERT DICKINSON JOWETT.

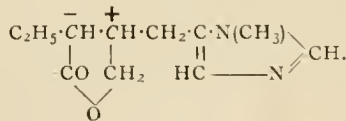
The author discussed the question as to the relationship between *pilocarpine* and *isopilocarpine*, and showed that the evidence on the whole favoured the view that the alkaloids were stereoisomerides. The views of Pinner on this subject (*Ber.*, 1905, xxxviii., 1570), namely, that the isomerism is not solely stereochemical, but structural, were shown to be open to objection. It was shown that if the alkaloids were stereoisomerides, *isopilocarpine* should be capable of conversion into *pilocarpine* by the same reagent which converts *pilocarpine* into *isopilocarpine*, whereas if they were structural isomerides this conversion would not take place.

By heating pure *isopilocarpine*, shown to be free from *pilocarpine*, with alcoholic potash, a mixture was obtained from which 80 per cent of pure *isopilocarpine* was separated, and from the mother-liquors, after re-crystallisation and conversion into the hydrochloride, a small quantity of pure *pilocarpine* was isolated. The identity of the latter was proved by the formation of the hydrochloride (m. p. 201° , $[\alpha]_D +92.8^\circ$), and of the nitrate (m. p. $177-178^\circ$).

It was thus shown that the alkaloids were almost certainly stereoisomerides, and may be represented by the following formula:—



Pilocarpine.

*isopilocarpine*.

CORRESPONDENCE.

ORIGINAL RESEARCH. SEPARATION OF CARBON.

To the Editor of the Chemical News.

SIR,—With regard to Brunner's recent communication to the Berlin Chemical Society on the separation of carbon from carbonic dioxide, kindly allow me to state that this fact was discovered by me many years ago, and published in the CHEMICAL NEWS. About the same time, I was the first to isolate, by means of magnesium, chemically pure zirconium (see Moissan, papers on Zirconium in the *Comptes Rendus*). I am too ill to look up the exact dates. —I am, &c.,

T. L. PHIPSON, Ph.D.

Casa Mía, Putney, S.W.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxl., No. 19, May 8, 1905.

A New Synthesis of Oxalic Acid.—H. Moissan.—The author effects a new synthesis of oxalic acid by using potassium hydride at a temperature of 80° . A current of dry carbon dioxide gas is passed over this, and combination takes place with great evolution of heat. The compound darkens, and the surface is covered with an almost black layer. It can be shown that the hydride has been transformed into a mixture of formate and oxalate of potassium. After treatment with sulphuric acid, prisms of oxalic acid are deposited, identical with those obtained by the ordinary known methods: $2\text{KH} + 2\text{CO}_2 = \text{K}_2\text{C}_2\text{O}_4 + \text{H}_2$.

A New Spectrum of Gadolinium.—G. Urbain.—On careful examination of a colourless solution of a gadolinium salt, the author discovers an absorption spectrum in the ultra-violet, represented by the following lines:—

β . $311.6-310.5$	A triple band, whose components are indistinct.
γ . $306.0-305.7$	Strong.
α . $305.6-305.5$	Very strong.
β . $305.4-305.0$	Very strong.

This spectrum is only observed in those earths which show the gadolinium line. It gradually weakens towards the europium heads of the fractionation and the terbium tails. The first experiments were made on gadolinia extracted from monazite sand, and were repeated with material extracted from xenotime and pitchblende.

Tribo-luminescence of Potassium Sulphate.—D. Gernez.—It was hitherto believed that the luminescence of potassium sulphate is produced at the moment when this salt dissolves from its vitreous and crystalline combination; the conditions necessary for this phenomenon being the formation of a double vitreous salt with sodium sulphate or an analogous salt. The light emitted is very fugitive, and in order to reproduce it all the operations must be re-commenced; and, finally, potassium sulphate alone does not emit light. The author makes a series of researches on these points, and finds that, in most cases, these assertions are not correct. Amongst other things he finds that crystals of potassium sulphate obtained from the most diverse sources are all luminescent when ruptured.

Action of Potassium-ammonium on Barium Bromide.—A. Joannis.—The author investigates the reaction taking place between potassium-ammonium and ammoniacal barium bromide, and finds that the following equation represents the principal reaction:— $\text{BaBr}_2 + 2\text{NH}_3\text{K} = 2\text{KBr} + \text{Ba}(\text{NH}_2)_2 + \text{H}_2$.

Electrolytic Reduction of Nitrocinnamic Acids.—C. Marie.—The meta- and paraitrocinnamic acids give on electrolysis in alkaline solution the corresponding azoacids. The position of the nitro or amino group has a very decided influence on the power of hydrogenation of the lateral chain. The para-derivatives give corresponding compounds of the hydrocinnamic series more easily than the meta-derivatives.

Action of Carbon Monoxide on Silver Oxide. Its Application for Detecting Traces of this Gas in the Atmosphere.—Henri Dejust.—On examining the action of carbon monoxide on silver oxide at ordinary temperatures and when quite dry, it is found that this oxide is immediately reduced to the metallic state with rise of temperature, $\text{CO}(\text{gas}) + \text{Ag}_2\text{O}(\text{solid}) = \text{Ag}_2 + \text{CO}_2 + 61.2 \text{ cal.}$ This reaction is sufficiently sensitive to make it possible to use it for the detection of traces of CO in the atmosphere.

Strontium Ammonium.—M. Roederer.—Calcium and barium when acted upon by ammonia gas give am-

monium compounds of formulae $\text{Ca}(\text{NH}_3)_4$ and $\text{Ba}(\text{NH}_3)_6$. An investigation of the similar strontium compound shows it to be analogous to the barium compound and have the formula $\text{Sr}(\text{NH}_3)_6$.

Osmosis through Silica Vessels.—G. Belloc.—The author makes a series of experiments on the causes of osmosis through quartz vessels, and finds that this phenomenon is due to more or less complete devitrification of the quartz, cellulose being formed at the high temperature at which the osmosis is observed. This explanation is in perfect accordance with M. Berthelot's researches.

A New Osmium Compound and an Osmium Reaction.—Pinerua Alvarez.—The author discovers a new osmium iodo-acid whose formula is probably $\text{I}_2\text{Os}_2\text{IH}$, and which when in solution has a bright emerald-green colour. He also finds that this compound can be used as an extremely delicate test for osmium. Thirty-seven ten thousandths part of metallic osmium can thus be detected.

Action of Alkalis on Aqueous Solutions of Acetol.—André Kling.—The author performs a series of experiments on the titration of acetol with various substances, and finds that towards alkalis this substance behaves as a pseudo-acid.

Saccharification by Malt of Artificial Starches.—Eug. Roux.—Artificial starches are saccharifiable by malt in the same way as natural starch. The same products of saccharification are given; that is to say, maltose and dextrans, which are formed in relative proportions depending on the temperature at which the malt acts. Under identical conditions of saccharification artificial starches give more maltose than natural starch, and the dextrans which are produced are more completely soluble in alcohol.

Use of Ammonium Metals in Organic Chemistry. Formation of Primary Amines.—Paul Lebeau.—The ammonium metals when reacting on the mono-substituted derivatives of the saturated carbides behave as hydrogenating agents on account of their transformation into amides. These latter bodies are immediately destroyed, and form the corresponding primary amines. The author shows that sodium amide can be employed for the fixation of the NH_2 group at a low temperature by the use of a suitable solvent.

MEETINGS FOR THE WEEK.

WEDNESDAY, 14th.—Chemical, 5.30. "Influence of various Sodium Salts on the Solubility of Sparingly Soluble Acids," by J. C. Philip. "The Dielectric Constants of Phenols and their Ethers Dissolved in Benzene and *m*-Xylene," by J. C. Philip and Miss D. Haynes. "Synthesis by means of the Silent Electric Discharge," by J. N. Collie. "The Ultra-violet Absorption Spectra of Benzene and certain of the Mono-substituted Derivatives," by E. C. C. Baly and J. N. Collie. "Association in Mixed Solvents," by G. Barger. "The Ultra-violet Absorption Spectra of Derivatives of Benzene—Part II. The Phenols," by E. C. C. Baly and Miss E. K. Ewbank. "The Action of Water on Diazo-salts," by J. C. Cain and J. M. Norman. "Synthesis of Substances Allied to Epinephrine," by G. Barger and H. A. D. Jowett. "A Precise Method of Determining the Organic Nitrogen in Potable Waters," by J. Campbell Brown. "Synthesis of 1:1-dimethyl- Δ^4 -tetrahydrobenzene," by A. W. Crossley and Miss N. Renouf. "Bromine in Solutions of Potassium Bromide," by F. P. Worley.

FRIDAY, 16th.—Physical, 8. "Ratio between Mean Spherical and Mean Horizontal Candle-power of Incandescent Lamps," by Dr. J. A. Fleming. "Electrical Conductivity of Flames," by Dr. H. A. Wilson. "Contact with Dielectrics and Exhibition of a Refractometer," by R. Appleyard. "The Pedulum Accelerometer—an Instrument for the Direct Measurement and Recording of Acceleration," by F. Lancaster. "New Form of Pycnometer," by N. V. Stanford.

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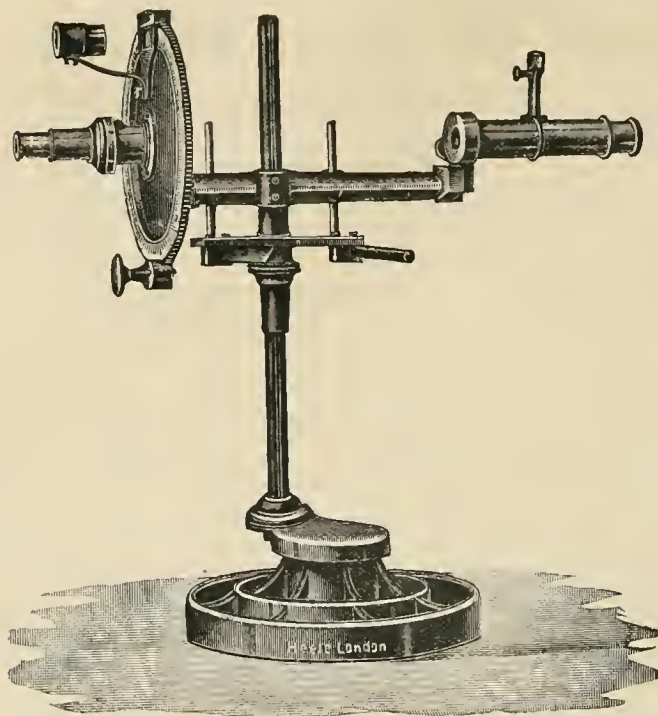
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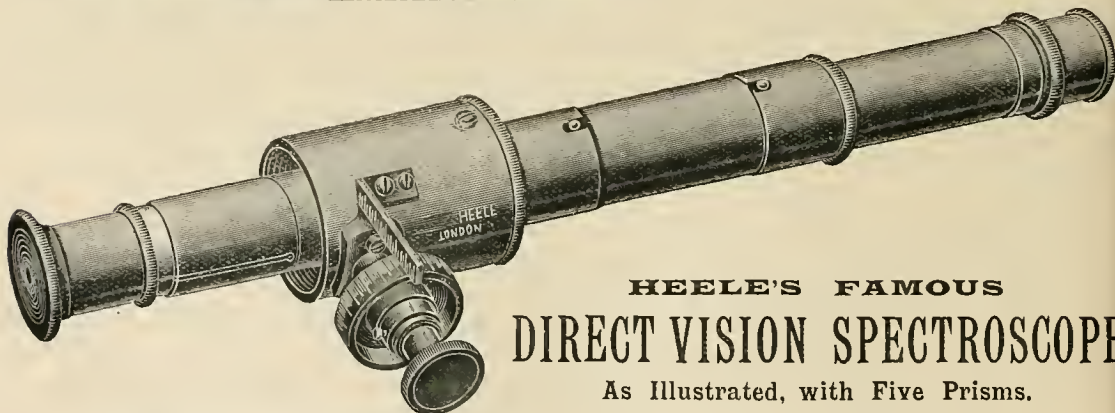
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THE CHEMICAL NEWS.

VOL. XCI., No. 2377.

THE RADIO-ACTIVITY OF THORIUM.

By O. SACKUR.

DURING the fractionation of a radium barium bromide mixture obtained by the usual analytical method from 2.5 tons of thorianite, O. Hahn found that the activity of the more soluble portion did not decrease steadily, but again increased after a series of fractionations (see CHEMICAL NEWS, vol. xci., p. 193). From these solutions by means of ammonia a very strongly active precipitate of some milligrammes was obtained; this precipitate was faintly luminous in the dark, and produced a bright light upon the platinum cyanide and zinc sulphide screen. By dissolving the precipitate in hydrochloric acid and precipitating with ammonium oxalate, the activity could be further concentrated; thus the radio-active body gives the same chemical reactions as thorium and the rare earths. As it gives off a strong emanation, both when solid and when dissolved, the idea occurred that it consisted of actinium, especially as Giesel had also obtained his strongest preparations from a radium barium mixture from pitchblende (*Berichte*, 1903, xxxvi., 342). The measurements of the rate of decay of the emanation performed by Hahn and me together showed, however, that it lost half its activity in a period of from fifty-two to fifty-five seconds, while the corresponding time for actinium-emanium amounts to 3.6 seconds. As, on the other hand, half the so-called duration of life of thorium emanation has been determined by Le Rossignol and Gimmingham (*Phil. Mag.*, July, 1904, 107) to be 51.2 seconds, and by Bronson (*Am. Journ. Sci.*, 1905, [4], 16, 185) to be fifty-four seconds, the emanation must be regarded as thorium emanation. This was also confirmed by the determination of the rate of decay of the induced activity, which indeed did not exactly decrease according to an exponential law like that produced by pure thorium emanation, but after some days reached a constant value, which, according to the experimental conditions, amounted to from 2 to 10 per cent of the initial activity. By subtracting this final value, however, we obtained a strictly logarithmic decrease of the induced activity, which gave a period of decay of 11.2 hours for the half value. (The measurements will be given in detail hereafter). Rutherford gave about eleven hours for the characteristic period of the induced activity produced by thorium emanation (*Journ. Chem. Soc.*, 1902, lxxx., 321).

Thus it is to be regarded as established that the body obtained by Hahn gives off thorium emanation; but since its power of emanation exceeded that of thorium about 250,000 times, as comparison experiments showed, it contains a new radio-active element which forms thorium emanation.

The possibility of the existence of such a substance has been considered by Elster and Geitel (*Physikal. Zeit.*, 1905, vi., 67) who, from the Baden-Baden "Ursprung," obtained a precipitate which gave off considerably more thorium emanation than an equal weight of thorium. They also found a somewhat slower rate of decay than corresponded to the induced activity produced by pure thorium emanation—a phenomenon which is also to be explained by a small residual activity. The nature and cause of this residual activity has not yet been explained.

The question now arises, what relation this new element bears to thorium—does it merely give in its radio-active transformation the same decay product of thorium, or is it to be regarded as the radio-active constituent of thorium?

In the first case we should have a hitherto unknown phenomenon, i.e., two different atoms in their spontaneous decay giving rise to the same decomposition product in much the same way as two different peroxides give up oxygen—and in the second case pure thorium must itself be inactive, its apparent radio-activity being caused by the presence of some constant impurity. This conjecture has often been expressed, and has been supported by the description of perfectly inactive thorium, both by Hofmann and Zerban (*Berichte*, 1903, xxxvi., 3093), and by Baskerville and Zerban (*Journ. Am. Chem. Soc.*, 1904, xxvi., 1642). Also the fact that the strongly active body can only be isolated in thorianite, the mineral which is by far the richest in thorium—it contains 78 per cent ThO_2 —argues in favour of this theory of admixture.

An artificial separation of a constantly active body from thorium has not as yet been effected, nor even a lasting concentration of the activity, and my experiments with this aim have not been successful; nevertheless, it does not seem to me to be superfluous to give a short account of them.

The traces of active substance found in the radium barium mixture can only be a small part of the whole quantity which was present in the thorianite, and was held by adsorption or solid solution in the barium sulphate. The greatest amount must be contained in the oxalate precipitate, which is formed in the soluble part of the mineral by the addition of ammonium oxalate after precipitation of the sulphide group with H_2S . This oxalate, which contains a few per cent of the rare earths besides thorium, and possess an activity of the order of magnitude of ordinary thorium, I chose for my original material. The first experiment consisted in the fractional sublimation of the chloride. The oxalate was ignited to oxide, mixed with charcoal and starch, and heated in the combustion furnace. At the same time a steady current of chlorine was led through the combustion tube. A very small quantity of a white chloride sublimed, which dissolved in water, and exhibited the reactions of aluminium, but was not active. Thorium chloride itself did not go over at the temperature employed (a red heat). As, moreover, by the sublimation of thorium chloride at a white heat, Baskerville (*Journ. Am. Chem. Soc.*, 1904, xxvi., 922) had not succeeded in proving any accumulation of the activity, the separation of an active constituent in this way does not appear to be possible.

The second experiment consisted in the imitation of the conditions under which the strongly active substance was obtained in the course of the analysis, namely, the employment of the already well-known power of adsorption of barium sulphate for radio-active substances. The oxalate was therefore converted into sulphate by evaporation with sulphuric acid, and barium hydroxide solution added drop by drop to the acid solution. The barium sulphate, which was precipitated, was strongly active, and its hydrochloric acid solution gave up considerable quantities of thorium emanation. The activity, however, did not remain constant, but rapidly decreased in such a way that after about four days it had sunk to half its value. On the other hand, the original thorium solution had lost half its power of emanation by once precipitating with barium sulphate, but regained it in the course of a few days. Thence it follows that the substance carried down with the barium sulphate is not the new constantly radio-active element, but thorium X, which Rutherford separated from thorium by means of ammonia (*Journ. Chem. Soc.*, lxxx., 837; *Zeit. f. Phys. Chem.*, 1902, xlii., 81). The barium sulphate precipitation thus affords a new method of separating this first decay product of thorium. The oxalate mixture from thorianite gave the same results as those I obtained with a thorium nitrate which I bought from the firm of Baird and Tatlock, of London, and concerning the origin of which I could learn nothing definite. In this case also by means of barium sulphate a separation of thorium X was effected.

Finally, I tried to separate the radio-active constituent electrolytically. Very little is known of the electro-

chemical properties of thorium and of its position in the potential series of the metals. It stands close to iron, but probably in consequence of the complex nature of its solutions it appears to be further removed from the noble metals than corresponds to its solution pressure. The electrolytic separation in larger quantities can be performed only with mercury cathodes. With platinum cathodes I obtained in neutral and very faintly acid nitrate and chloride solution, as well as from the hot solution of the ammonium double oxalate, a small metallic grey precipitate which dissolved in acids, hydrogen being evolved; but possibly this did not consist of thorium, but of another of the metals contained in the oxalate mixture. On the anode in nitric acid solution there always formed a thin film of lead peroxide, an impurity which commercial thorium nitrate also contains. Pegram also had shown its presence in the preparation he used (*Phys. Review*, 1903, xvii., 423).

In my experiments I always used platinum electrodes and currents of 3 to 4 volts and some tenths of an ampère. The electrodes, after interrupting the current and washing out the solution, were treated with warm hydrochloric acid, and this was evaporated as quickly as possible in clock glasses. The residues, even if they were hardly ponderable quantities, as, for example, with anodes in chlorides solutions and cathodes in acid solutions, were always strongly active, but their activity diminished very rapidly. The measurements of the activity were performed in a brass vessel with insulated brass rod, in which the saturation current was determined electrometrically. The decrease never followed an exponential law, being much greater in the first hours than afterwards. According to the experimental conditions, from the first measurement onwards the activity sinks in two or more hours to half its value. After one day it always remains constant for several weeks, and is then mostly somewhat greater than corresponds to an equal weight of thorium. If every radio-active substance decays according to an exponential law, a simultaneous electrolytic separation of several substances must occur, their time laws being superposed, which conceals the simple logarithmic course. From the rate of decay of the activity on the electrodes it follows that no appreciable separation of a constantly active substance occurs, but a separation of induced activity, or as Rutherford expresses it, of decomposition products of thorium. V. Lerch also by electrolytic experiments was led to the conclusion that the induced thorium activity is not of a simple, but complex nature (*Ann. d. Phys.*, 1903, [4], xii., 745).

In chloride and oxalate solutions these induced activities go chiefly to the cathode, while the anode only becomes feebly active; in neutral and feebly acid nitrate solution they go equally to cathode and anode, and in strongly acid nitrate solution almost entirely to the anode. Thus they behave electro-chemically like a metal which is inclined to form peroxides, *i.e.*, something like lead.

These results do not agree completely with the results of Pegram (*loc. cit.*). Pegram electrolysed thorium nitrate solutions and measured the decrease of activity of the electrodes. He found only the anode active, and this activity decreased to half its value in eleven hours according to the known exponential law which holds for thorium induction. On the other hand, by addition of copper to the solution he obtained a copper precipitate which lost half of its activity in ten minutes; a precipitate of silver chloride produced in the solution lost half its activity in eighty minutes. Thus it is clear that in this case the rates of decay of the induced thorium activity can assume the most different values.

I have repeated my electrolytic experiments with the above mentioned commercial thorium preparation and have obtained exactly the same phenomena, and also with very dilute solutions of the strongly active substance, *e.g.*, the filtrate of the oxalate precipitate. From its concentrated solutions, on the other hand, as Hahn has already found, strongly active preparations are obtained on both electrodes; their activity increases for several days,

and their solution gives off thorium emanation. The induced activity is here masked by the separation of the much more strongly active substance.

Even if the electrolytic experiments with platinum electrodes have led to no separation of a constantly radio-active constituent, they have nevertheless shown that solutions of thorium from thorianite as well as from other minerals behave on electrolysis like diluted solutions of the new strongly radio-active element. Thus this seems to be present in them in small quantities and to cause their radio-activity. Therefore the above conclusion, which has already been established, was confirmed by my experiments, *viz.*, that pure thorium is itself not active, and owes its activity only to the admixture of a strongly active element, which is chemically extraordinarily similar to it.

I owe hearty thanks to Sir William Ramsay for his continued kind interest and many suggestions.—*Berichte*, 1905, xxxviii., 1756.

ELECTRICALLY HEATED CARBON TUBE FURNACES.*

PART I.

By R. S. HUTTON, M.Sc., and W. H. PATTERSON, B.Sc.

It is surprising when the importance of the subject is considered, how very little laboratory work has been done with the electric furnace under properly adjusted and fixed temperature conditions in those higher regions of temperature where the electrical is practically the only possible method of heating. Up to 1300° C. the furnaces in which an electric current passes through a nickel or platinum wire have fully proved their usefulness, whilst in the case of experiments of short duration platinum wire or foil heating coils have been employed for temperatures up to about 1600° C., but seemingly suffer very rapid deterioration when used for any length of time under these conditions. The iridium tube furnace of Nernst and Heraeus, even where its high cost is not prohibitive, seems to be unsuited for all but the most delicate of experiments, although with its temperatures up to 2100° C. can be attained (*W. Nernst, Trans. Amer. Electrochem. Soc.*, 1903, iii. 75; *Zeit. Elektrochem.*, 1903, ix., 623; *W. C. Heraeus, Zeit. Angew. Chemie*, 1905, 49-53). Mention might also be made of the oxy-hydrogen furnace of Moissan (*Ann. de Chim. et de Phys.*, 1901, Ser. 7, xxiv., 289) and the oxy-retort-graphite and water-gas furnaces of Victor Meyer and H. Biltz (*V. Meyer and M. von Recklinghausen, Berichte*, 1897, xxx., p. 1926; *H. Biltz, Z. Physik. Chem.*, 1896, xix., 385), since these have served for somewhat delicate work, but of course, in these cases the temperature conditions are not so fixed as when electrical heating is employed.

Several workers have recently employed furnaces constructed with a carbon tube through which an electric current is passed (*F. Haber, "Grundriss der Techn. Elektrochemie," Munich*, 1898, p. 380; *Lummer and Pringsheim, Ber. Deutsch. Phys. Gesell.*, 1903, 3; *H. N. Potter, U.S.A. Patents 715,506 to 715,509, Dec. 9, 1902, and 756,891, April 12, 1904*). This type of furnace seems to be the most readily available for the very highest temperatures; despite some inherent disadvantages due to the presence of carbon, it is capable of very wide application.

The authors do not propose to claim any superiority† of their types of carbon tube furnaces over those constructed by other workers. As, however, they have been able to get satisfactory results with a very simple type of con-

* A Paper read before the Faraday Society, April 4, 1905.

† In particular, the construction of some of the furnaces of Mr. H. N. Potter is obviously more perfect in many of the essential details; although probably they could not very easily be made and installed for ordinary laboratory work.

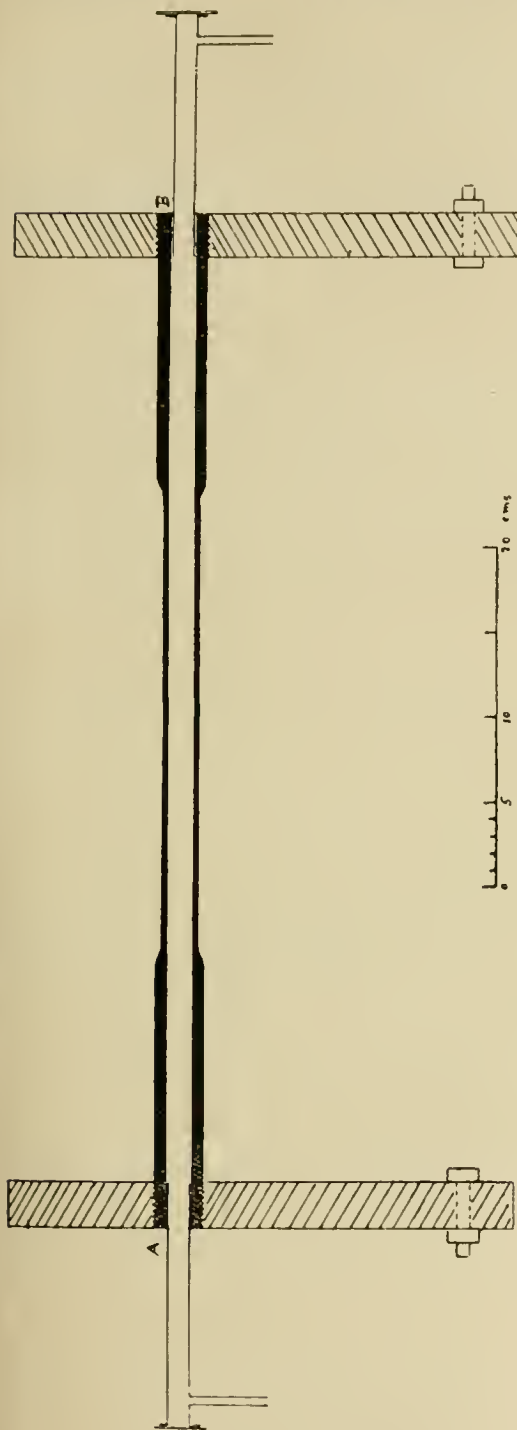


FIG. 1.—GRAPHITE TUBE FURNACE.

(FIG. 1.—The tube is bored and turned from a solid rod, and is screwed at the ends into graphite plates, 2.6×5.2 c.c., which are clamped to copper holders not shown. The glass extensions, which are fixed into the graphite

tube at A and B by asbestos, serve for the passage of gas through the tube; the plate-glass ends enable the progress of the experiment to be observed from either end. The central portion of the tube is surrounded with carborundum, or other heat-insulator, not shown in the figure. The material to be heated is placed in small carbon boats which are advanced to near the centre of the tube).

struction, they thought that a brief account of their preliminary work in this direction might be of some general interest.

General Considerations.—The most important points in the construction of carbon tube furnaces are, firstly, the provision of a satisfactory device for leading the current to the ends of the tube, and, secondly, the protection of the tube from contact with the air or other material capable of reacting with the carbon to burn it away. It is, moreover, a very great advantage to closely jacket the tube with some substance which, whilst not tending to combine with the carbon, forms an efficient heat-insulator. Even with the most carefully constructed system of exterior concentric tubes with intermediate gas spaces, a great amount of heat is carried away by convection currents in the gases, and consequently much more power has to be expended in the tube to attain any required degree of temperature than when the tube is closely jacketed by some material of low thermal conductivity.

The connections at the ends of the tubes should be so constructed as to remain sufficiently cool to prevent any oxidation of that part of the carbon which is exposed to the air. Moreover, provided the ends are kept cool, it is an easy matter to make a gas-tight joint for the passage of any desired gas through the tube.

Graphite Tube Furnace.—The first furnaces made use of were constructed of Acheson graphite, a tube being bored from a solid rod of about 3 c.c. diameter, as shown in Fig. 1. Doubtless, when only a few experiments have to be carried out, this method of construction has its advantages. Blocks and rods of graphite are so frequently required in experimental electric furnace work, that the necessary material is almost sure to be at hand in any laboratory where such furnaces are wanted; whereas the methods of construction, to be described later, require a special provision of carbon tubes of the particular dimensions suitable for the current and power available. The tube was screwed to graphite plates, which served to lead in the current, the graphite plates being held between thick copper clamps, mounted on stands capable of sliding on a smooth plank; to these clamps the cables were connected. One of the sliders was balanced so as to more easily admit of expansion of the tube without fear of breakages. For heat insulation the graphite tube was surrounded with magnesia, or, later, carborundum held in place by brickwork not shown in the figure. On account of the very great shrinkage of calcined magnesia this material was not found satisfactory as a jacketing material; after the tube has been in use for a short time fissures are formed, which allow the air to come into contact with the carbon, and consequently considerably curtail its life; probably by using fused magnesia in the form of powder, better results could be obtained, and experiments in this direction are now in progress.

Both for these graphite tubes and also for the forms of furnace described later, carborundum has been found to be an excellent jacketing material. It is a fairly good heat-insulator, and has the advantage of being a reducing agent, consequently protecting the carbon from burning away.* This material has been used in a fine granular condition (the grains just passing through a sieve 180 meshes to the linear inch). So soon as the graphite has attained a fairly high temperature these grains frit

* For instance, one of the smaller tubes, after ten or twelve experiments, in nearly all of which it had been heated well above the melting-point of platinum, was found to have altered only to a quite insignificant extent in internal and external diameter.

together, forming an adherent, tube-shaped jacket around the graphite, which serves to strengthen and protect it.

The material to be heated in this furnace is placed in a small boat made of graphite or ordinary agglomerated carbon, the bottom of the boat being shaped so as to touch the tube at only a few points, and thus not itself to conduct any appreciable amount of the current.

The temperature is estimated by having a number of small carbon holders on each side of the boat, with pieces of various metal wires placed upright in them.*

At approximately the melting-point of the metal the wire sinks and disappears from view. For higher temperatures little cones of pure alumina or magnesia have been used, but more recently an optical pyrometer has been obtained, which it is hoped will prove very serviceable for experiments of this kind. The thicker ends of the graphite tube and the graphite plates get too hot to admit of a rubber or cork stopper being used; the glass tubes which serve for the gas inlet and outlet were therefore fixed with a plug made of fine asbestos string.

(To be continued.)

ON A NEW TYPE OF ELECTRIC FURNACE, WITH A RE-DETERMINATION OF THE MELTING-POINT OF PLATINUM.†

By J. A. HARKER, D.Sc., Joule Scholar of the Royal Society,
Assistant at the National Physical Laboratory, Teddington.

(Continued from p. 263.)

IX. Properties of the Thermo-junctions.

T₁₄ is a unique specimen in that it consists in what is probably the first wire investigated thermo-electrically, made from the large mass of exceptionally pure platinum-iridium prepared by Mr. Matthey for the construction of the "étalons prototypes" of the kilogramme and metre for the International Commission of Weights and Measures in 1886. The analysis made by Stas and by Ste.-Claire Deville of two samples of this alloy gave a mean value—

Pt =	89.841
Rh =	0.135
Ru =	0.034
Fe =	0.066
Ir =	0.880
	99.956

all the constituents being determined directly, and not by difference. This alloy serves as a standard of comparison for all junctions of platinum-iridium wire.

T₉ and M₉ are specimens supplied commercially to the laboratory at different dates, the products being stated to be of high commercial purity. M₅ is representative of several alloys of a similar character, not definitely called "pure," but sold simply as 10 per cent alloy, the quality of the platinum wire forming the other side of the junction being also unspecified. M₁ and T₂₀ are 10 per cent rhodium alloys of similar quality bought at different times, and T₂₁ is a junction composed of the same alloy of iridium as the sample used in junction T₉, against the rhodium alloy used in T₂₀. It will be noticed that the sensitiveness of this junction is only about a quarter of that of a pure platinum-rhodium alloy against platinum, and that it *diminishes* fairly rapidly with increase of temperature. In the experiments with this junction the melting-point was taken of a small piece of pure platinum, which was twisted several times round the junction of the two

wires. After melting, this formed into a large drop, which surrounded the point of contact of the two alloy wires.

The specimens of platinum used in making up the junctions were not specially analysed at the laboratory. Five separate samples were utilised. It is, however, certain that the specimens used in the first four junctions and in the experiments with T₂₁ were of very high quality, but it was found that the wire used in M₁ and M₅, when tested thermo-electrically against that of T₁₄ and T₁₅, gave an appreciable thermo-electric force at the higher ranges, and it is probably owing to this cause, and not to any lowering of the freezing-point of the platinum by impurities, that the two low values 1692° and 1695° are due.

X. Result of the Determinations.

Rejecting, therefore, these two determinations, the agreement between the remaining seven junctions is of such a character that it appears highly probable that the value 1710° C. represents to within 5° C. the melting-point of platinum as determined by the thermo-electric method.

It may be objected, however, that in spite of the good agreement of determinations made with so many junctions, whose curves of E.M.F. against temperature differ so widely from one another, both as regards slope and degree of curvature, the extrapolation of a formula, which is only known to hold over a range of about 800° C., to cover an additional 500° C., is unjustifiable, and that it is quite possible an intermediate point on the extrapolated part of the curves might not show such good agreement.

XI. Doubt as to Validity of Extrapolation. Confirmation of Formula at Melting-point of Nickel.

It was therefore decided to determine the freezing-point of nickel with some of the junctions as control. Table IV. gives the result of these determinations summarised. The nickel used was a very pure sample of nickel berries from Brunner, Mond, and Co., made by the Mond process, and found—by analyses made at the laboratory by Dr. Carpenter—to contain 99.6 per cent nickel before fusion. Three careful experiments made in an electric furnace in a reducing atmosphere by the ordinary crucible method with junction N. P. L. 2 gave 1428°, 1429°, and 1427° C.; a previous determination made on the same material by Dr. Carpenter on a much larger scale, using a wind furnace and a junction from the same stock of wire as T₉, gave 1427° C. as the temperature of the commencement of solidification. In both these determinations the junctions were protected by thin fire-clay tubes. The two perfectly independent results agree within far less than the probable error.

Some further observations show that it was quite easy to obtain a well-defined melting-point of a small granule of nickel round which the junction was wrapped, without sensible oxidation of the metal, in the new type of furnace used for the platinum points. Preliminary experiments with different conditions of immersion, &c., showed that the melting-point thus obtained agreed satisfactorily with the standard method even when no special gas was passed through the furnace, and that any nickel volatilised or diffused into the thermo-junction wires only affected these for a few millimetres of their length over the part actually in contact with the metal. The results obtained with the six junctions used are shown in Table IV.

XII. Final Value for Melting-point of Platinum.

It will be noticed that the junction T₂₀, which reads 14° C. low at the platinum point, is low by a similar amount at the nickel point, but that the first four junctions given in the table agree fairly well, those which are low at the platinum point being also low near 1400° C.

These data furnish an answer to the possible objection which might be urged against the method that the comparative agreement at 1700° C. is really fortuitous.

The value given by these experiments for the melting-point of platinum,—

$$1710^{\circ} \pm 5^{\circ} \text{ C.},$$

* The practical constancy of temperature throughout the central portion of the tube was determined by having a number of small boats containing projecting nickel wires at regular intervals, and noting, when the temperature was slowly raised, that those in the central 15 c.c. melted at very nearly the same time.

† A Paper read before the Royal Society, April 13, 1905.

TABLE IV.—Melting-points of Nickel and Platinum Compared.
(Most probable value for Nickel $1427^{\circ} \pm 3^{\circ} \text{C.}$, for Platinum $1710^{\circ} \pm 5^{\circ} \text{C.}$).

No. of junction.	Date of experiments.	Number of experiments on nickel.	Mean value.	Divergence from probable value.	Platinum point on same junction.	Divergence from probable value.
N. P. L. 3	1905 January 25, J. A. H. . . .	3	1428	+1	1712	+2
T ₉	1904— November 21, H. C. H. C. (crucible method) . . .	1	1427	+0	1711	+1
T ₁₅	1905— January 28	2	1420	-7	1707	-3
T ₁₄	" 28	5	1422	-5	1705	-5
T ₂₀	" 31	4	1412	-15	1696	-14
T ₂₁	February 6	5	1419	-8	1712	+2

is very considerably lower than the previously accepted numbers. Of these earlier determinations undoubtedly the most important is the one made by Violle, which was a calorimetric estimation, depending on the extrapolation of a value determined for the specific heat of platinum from 1200°C. upwards. Violle's value is usually given as 1780°C. In his own memoir he says that if this value is in error it will probably be found to be too high, as platinum is a metal which softens gradually, and when in this state the specific heat will probably be intermediate between that of the solid and the liquid, thus leading to an error in this direction.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, June 1st, 1905.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Bryce Chudleigh Burt, B.Sc., Port of Spain, Trinidad, B.W.I.; Joseph Morgan Davey, Shetone House, Briton Ferry, Glam.; Herbert Drake Law, B.Sc., 152, Brixton Road, S.W.; Thomas Rigby, 23, The Square, Fairfield, Manchester; Arthur Gough Ruston, B.A., B.Sc., 244, Oxford Road, Reading.

Of the following papers, those marked * were read:—

*99. "The Constituents of the Seeds of *Hydnocarpus Wightiana* and of *Hydnocarpus anthelmintica*. Isolation of a Homologue of Chaulmoogric Acid." By FREDERICK BELDING POWER and MARMADUKE BARROWCLIFF.

The fatty oils from the seeds of *Hydnocarpus Wightiana* (Blume) and *H. anthelmintica* (Pierre) have long been used in Western India and in China respectively for the same medicinal purposes for which chaulmoogra oil is employed. In view of this fact and of the interesting results obtained during the investigation of chaulmoogra seeds, from *Taraktogenos Kurzii*, King (Power and Gornall, *Trans.*, 1904, lxxxv., 838), the authors have examined the seeds of these two species of *Hydnocarpus* with especial regard to the constituents of their fatty oils.

The seeds of *H. Wightiana* yielded, on expression, 32.4 per cent, and by extraction with ether 41.2 per cent of oil. The expressed oil had the following characters:—M. p. $22-23^{\circ}$; sp. gr. 0.958 at 25° ; $[a]_D + 57.7^{\circ}$ in chloroform; acid value, 3.8; saponification value, 207; iodine value, 101.3.

The seeds of *H. anthelmintica* gave, on expression, 16.3 per cent, and by extraction with ether 17.6 per cent of oil. The expressed oil had the following characters:—M. p. $24-25^{\circ}$; sp. gr. 0.953 at 25° ; $[a]_D + 52.5^{\circ}$ in chloroform;

acid value, 7.5; saponification value, 212; iodine value 86.4.

The authors found that these two oils very closely resemble chaulmoogra oil (from *Taraktogenos Kurzii*) both in physical characters and in composition, consisting chiefly of the glyceryl esters of chaulmoogric acid $\text{C}_{18}\text{H}_{32}\text{O}_2$, and a lower homologue of the same series, which was isolated from both oils, and also from chaulmoogra oil. The new acid has the formula $\text{C}_{16}\text{H}_{28}\text{O}_2$, and is designated *hydnocarpic acid*; it crystallises from alcohol in glistening leaflets, melting at 60° , and having $[a]_D + 68^{\circ}$ in chloroform. It is an unsaturated acid, containing only one ethylenic linking, and therefore possesses a closed carbon ring.

Methyl hydnocarpate, $\text{C}_{15}\text{H}_{27}\text{CO}_2\text{Me}$, is a colourless oil, which boils at $200-203^{\circ}$ (corr.) 19 m.m., and solidifies when cooled, forming crystals which melt at 8° . It has $[a]_D + 62.4^{\circ}$ in chloroform. *Ethyl hydnocarpate*, $\text{C}_{15}\text{H}_{27}\text{CO}_2\text{Et}$, boils at 211° (corr.) 19 m.m., is a colourless oil, and has $[a]_D + 51.6^{\circ}$ in chloroform. *Hydnocarpamide*, $\text{C}_{15}\text{H}_{27}\text{CO}\cdot\text{NH}_2$, forms needles from alcohol. It melts at $112-113^{\circ}$ and has $[a]_D 30^{\circ} + 70.2^{\circ}$ in chloroform.

The oil of *Hydnocarpus Wightiana* appears to contain, besides the above-mentioned acids, a very small proportion of an acid or acids belonging to the linolic or linolenic series. The oil of *Hydnocarpus anthelmintica*, on the other hand, contains, as minor constituents, small amounts of oleic and palmitic acids.

*100. "The Constituents of the Seeds of *Gynocardia odorata*." By FREDERICK BELDING POWER and MARMADUKE BARROWCLIFF.

Prior to the year 1900 it was generally believed that the chaulmoogra oil of commerce was obtained from the seeds of *Gynocardia odorata* (R.Br.). More recently, however, it has been recorded by Mr. E. M. Holmes (*Pharm. Journ.*, 1900, lxi., 522; 1901, lxvi., 596), on the authority of Dr. Prain, Director of the Botanic Survey of India, that chaulmoogra oil is afforded by the seeds of *Taraktogenos Kurzii* (King), these seeds having evidently been wrongly referred to the genus *Gynocardia*. Moreover, one of the authors and Mr. F. H. Gornall (*Trans.*, 1904, lxxxv., 838) have shown that the oil from authentic *Taraktogenos* seeds is identical in physical character and composition with the chaulmoogra oil of commerce. The authors now state conclusively that the oil known in European commerce as "chaulmoogra oil," and sometimes as "gynocardia oil," could never have been obtained from the seeds of *Gynocardia odorata*, since the oil from these seeds, at the ordinary temperature, is a liquid, whereas, chaulmoogra oil is solid (m. p. $22-23^{\circ}$). Furthermore, chaulmoogra oil is optically active, and consists chiefly of the glyceryl esters of acids of the chaulmoogric series (compare Power and Gornall, *loc. cit.*, and the preceding abstract), whereas the oil from *Gynocardia* seeds is optically inactive, and contains neither chaulmoogric acid nor its homologues.

The seeds of *Gynocardia odorata* used in this investigation were collected in Sylhet, Assam, and were of undoubted genuineness. They yielded, on expression, 19.5

per cent, and by extraction with ether 27.2 per cent of oil, which had a light yellow colour and an odour like that of linseed oil. The expressed oil had the following characters:—Sp. gr., 0.925 at 25°; acid value, 4.9; saponification value, 197; iodine value, 152.8. It was found to consist of the glyceryl esters of the following acids:—(1) Linolic acid, or isomerides of the same series, constituting the largest proportion of the oil; (2) palmitic acid in considerable amount; (3) linolenic and isolinolenic acids, the latter preponderating; and (4) oleic acid in relatively small amount.

In addition to the fatty oil, *Gynocardia* seeds contain, as has previously been shown (Power and Lees, *Trans.*, 1905, lxxxvii., 349), 5 per cent of a crystalline cyanogenetic glucoside, gynocardin, $C_{13}H_{19}O_9N \cdot 1\frac{1}{2}H_2O$, and a hydrolytic enzyme, gynocardase.

*101. "The Relation of Ammonium to the Alkali Metals. A Study of Ammonium Magnesium and Ammonium Zinc Sulphates and Selenates." By ALFRED EDWIN HOWARD TUTTON.

The results of this investigation are remarkably similar to those previously published (*Trans.*, 1903, lxxxiii., 1049) for ammonium sulphate and its relations to the analogous sulphates of potassium, rubidium, and caesium, and the following conclusions have been deduced.

With regard to the three properties which refer to the fundamental structural unit of the crystals, namely, the molecular volume, the topic axis (the relative distances apart, along the three crystallographical axes, of the centres of contiguous structural units), and the molecular refraction, it is shown that the ammonium salt of any double salt group of the series behaves almost exactly like the rubidium salt. The same was previously shown to be true of ammonium sulphate in the simple salt series.

With respect to the properties of the crystals themselves, they resolve themselves into two classes. Those of the one category follow the order of the molecular weights, and include the densities, the rotation of the optical ellipsoid about the symmetry axis of the crystals, and the specific refraction and dispersion. In those of the other class, the ammonium salt occupies positions varying from one quite close to the rubidium salt to another nearer to the caesium salt, and to this class belong the interfacial angles, the monoclinic axial angle, the three refractive indices (corresponding to the three axes of the optical ellipsoid), the mean refractive index for the whole crystal, the double refraction, and the axial ratios of the optical ellipsoid.

These definite results afford ample scope for speculation as to the special conditions which permit of the replacement of two atoms of the alkali metal potassium by ten atoms of the two ammonium groups, with no more effect on the crystallographical characters and on the dimensions and properties of the structural unit than if a mere exchange for two other analogous metallic atoms had occurred.

*102. "Camphorylazoimide." By MARTIN ONSLOW FORSTER and HANS EDUARD FIERZ.

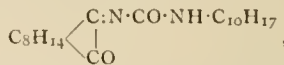
Camphorylazoimide, C_8H_{14} , precipitated from

a solution of camphoryl-ψ-semicarbazide nitrate by sodium nitrite, crystallises from alcohol in long, flattened, transparent prisms, which retain their lustre when protected from light, becoming opaque on exposure to sunlight during a few minutes; it melts at 67°, is volatile in steam, and decomposes on heating without explosion. Concentrated sulphuric acid, alcoholic alkali hydroxides, and an acid solution of stannous chloride liberate two-thirds of the nitrogen quantitatively, and reduction with zinc and acetic acid converts the substance into aminocamphor.

α-Iminocamphor, C_8H_{14} , produced when alcoholic

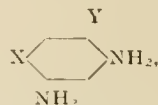
ammonia and alkalis act on the azoimide, is an unstable

solid, which rapidly undergoes decomposition on exposure to air. Dilute acids resolve it quantitatively into ammonia and camphorquinone, whilst bornylcarbimide converts it into the stable carbimide,—



*103. "Influence of Substitution on the Formation of Diazoamines and Aminoazo-compounds. Part III. Azo-derivatives of the Symmetrically Disubstituted Primary Meta-diamines." By GILBERT THOMAS MORGAN and WILLIAM ORD WOOTTON.

In 1902, one of the authors showed, from a study of three primary meta-diamines having the general formula—

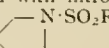


that these substances yield azo-derivatives, although much less readily and in smaller yield than those meta-diamines containing a free para-position with respect to one of the amino-groups. This investigation has now been extended to a larger series of these bases containing chlorine, bromine, iodine, and nitroxyl substituents, and the results obtained lead to the following conclusions:—(1) The course of the condensation is not materially affected by an increase in the atomic weight of the halogen substituent, although the colour of the azo-compound deepens considerably; (2) the yield of the azo-derivative is greatly increased when a nitro-group is present in the nucleus of the diazonium salt, and to a less extent when this substituent is present in the molecule of the diamine.

The following new diamines have been prepared and characterised:—6-Chloro-4-nitro-m-phenylenediamine, 6-bromo-4-nitro-m-phenylenediamine, and di-iodo-m-phenylenediamine.

*104. "Diazo-derivatives of Monoacylated Aromatic Para-diamines." By GILBERT THOMAS MORGAN and FRANCES MARY GORE MICKLETHWAIT.

The authors having previously observed that benzene-sulphonyl-*p*-phenylenediamine and camphor-β-sulphonyl-*p*-phenylenediamine when treated with nitrous acid yield

diazo-anhydrides of the type C_6H_4 , now show

that this condensation occurs with other aromatic para-diamines, and benzene-sulphonyl-2:5-tolylenediazoimide, benzene-sulphonyl-2:5-*p*-xylylenediazoimide, and benzene-sulphonyl-1:4-naphthylenediazoimide have been prepared.

A study of the diazo-derivatives of other monoacylated para-diamines indicates that the formation of similar cyclic diazoimides does not occur with the formyl, acetyl, succinyl, and benzoyl derivatives of *p*-phenylenediamine. From the first two members of this series, ill-defined nitrosoamines of the type $R \cdot CO \cdot NH \cdot C_6H_4 \cdot NH \cdot NO$ have been produced, whilst benzoyl-*p*-phenylenediamine, when diazotised and treated with cold aqueous potassium carbonate, yields a remarkably stable diazonium carbonate, $C_6H_5 \cdot CO \cdot NH \cdot C_6H_4 \cdot N_2 \cdot HCO_3$. This substance, which is very sparingly soluble in water, dissolves with effervescence in cold dilute mineral acids, readily condenses to form azo-derivatives with phenols and aromatic amines, and when boiled with acidified water yields benzoyl-*p*-aminophenol (m. p. 205–207°).

Benzoyl-*p*-phenylenediamine also gives rise to a sparingly soluble yellow diazonium nitrite,—



which readily yields azo-derivatives.

DISCUSSION.

The PRESIDENT congratulated the authors on having, as far as he knew, been the first to isolate in a definite solid

form a diazonium carbonate and nitrite. In many diazo-decompositions, and notably in the transformation of β -naphthylamine into β -nitronaphthalene, it was necessary to assume the intermediate formation of a diazonium nitrite, but such a salt had not hitherto been isolated.

*105. "The Significance of Optical Properties as Connoting Structure:—Camphorquinone—Hydrazones—Oximes: a Contribution to the Theory of the Origin of Colour and to the Chemistry of Nitrogen." By HENRY E. ARMSTRONG and WILLIAM ROBERTSON.

The authors discuss the significance of optical properties generally with reference to the structure of camphorquinone and the oximes and hydrazones derived therefrom; they apply the conclusions arrived at to the general problems of the connection between optical attributes and structure, ultimately expressing the view that there is not a tittle of proof in support of the Hantzsch-Werner hypothesis of isomerism among nitrogen compounds. Several new "hydrazones" are described.

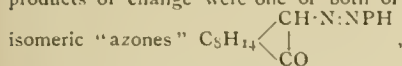
DISCUSSION.

Dr. LAPWORTH said that Mr. Hann and he had not intended to offer any definite expression of opinion as to the correctness of Betti's formulæ for the isomeric hydrazones of camphorquinone, although they had certainly not avoided giving the impression that they approved of them.

In reality, his own opinion had been, firstly, that the substance melting at 180° was the true hydrazone—



and that the ferric chloride colouration it affords was due to an impurity not easily removed, and secondly that the products of change were one or both of the two stereo-



However, as he and his colleague could not shake Betti's evidence nor adduce any direct evidence in favour of the other view, they did not find fault with this investigator's formulæ and adopted the terms first used by him.

*106. "Solubility as a Measure of the Change undergone by Isodynamic Hydrazones. (1) Camphorquinone-phenylhydrazone. (2) Acetaldehyde-phenylhydrazone." By WILLIAM ROBERTSON.

The applicability of the method of determining the variation in solubility with time as a means of estimating the proportions of isodynamic substances in solution has been further shown by extending the investigation to hydrazones. The relative proportion present in the equilibrium mixture in the case of the phenylhydrazone of camphorquinone is found to be about 9 : 1.

*107. "The Design of Gas-regulators for Thermostats." By THOMAS MARTIN LOWRY.

Tests are described of seven different regulators. Two new patterns are described. By means of one of these the temperature of a bath of water may be maintained within $\pm 0.01^\circ$ during several weeks, the average fluctuation being about $\pm 0.002^\circ$.

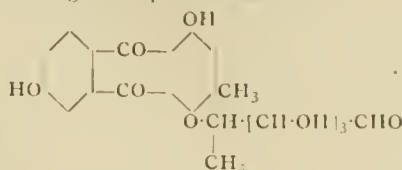
DISCUSSION.

Sir W. RAMSAY suggested the use of a Bourdon gauge tube and a small-sized regulator.

*108. "The Constitution of Barbaloin." (Part I.) By HOOPER ALBERT DICKINSON JOWETT and CHARLES ETTY POHLE.

The authors reviewed the previous work on this subject, and showed that there exist two very different views as to the empirical formula of barbaloin. The older formula, $\text{C}_{16}\text{H}_{18}\text{O}_7$, proposed by Tilden in 1875 (or the very slightly different one, $\text{C}_{16}\text{H}_{16}\text{O}_7$, of Groenewald) has been generally accepted until quite recently, when Léger, in 1902, adopted

the formula $\text{C}_{21}\text{H}_{20}\text{O}_9$, and suggested that the constitution of barbaloin might be represented as follows:—



The more recent work of Aschan has tended to confirm the older formula, $\text{C}_{16}\text{H}_{18}\text{O}_7$, rather than that of Léger.

The authors have made a number of analyses and molecular weight determinations of carefully purified barbaloin and tribromobarbaloin, and their results agree best with Tilden's formula. They have been unable to confirm Léger's statements respecting the decomposition of barbaloin with sodium peroxide, but have proved the correctness of Oesterle's results.

Tetra-acetyltribromobarbaloin, $\text{C}_{24}\text{H}_{23}\text{O}_{11}\text{Br}_3$, which was obtained in well-defined yellow needles, melts at 135° .

Tribromobarbaloin, and probably barbaloin, therefore, contain four hydroxyl groups. A number of experiments on the action of various reagents on barbaloin and tribromobarbaloin were recorded.

DISCUSSION.

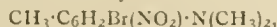
Prof. TILDEN remarked that much of the confusion existing in the work by earlier investigators of aloin arose from the fact that it was not fully recognised that the crystalline substances obtained from the several varieties of the drug were not identical. About 1870 this confusion began to be cleared away, and he believed that he was responsible for the application of the names barbaloin, socaloin, &c., to the several substances then recognised as distinct. The mistaken idea that the aloins are glucosides probably arose from the fact that most of them reduce Fehling's solution. He did not propose to resume the study of these substances, but wished success to Dr. Jowett and his colleague in their investigation.

*109. "Influence of Substitution on the Formation of Diazoamines and Aminoazo-compounds. Part IV. 5-Bromo-as(4)-dimethyl-2 : 4-diaminotoluene." By GILBERT THOMAS MORGAN and ARTHUR CLAYTON.

The base, 5-bromo-as(4)-dimethyl-2 : 4-diaminotoluene (m. p. 40°), has been prepared with the object of investigating the action of diazonium salts on a partially alkylated meta-diamine containing substituents in the two para-positions with respect to the aminic nitrogen. The orientation of the substituents in this diamine was determined by preparing the substance by the following alternative methods:—

1. Dimethyl-*p*-toluidine was converted into 2-nitrodimethyl-*p*-toluidine, and this compound, when successively reduced, acetylated, and brominated, yielded an acetyl-bromo-as(4)-dimethyl-2 : 4-diaminotoluene (m. p. 163°), from which the bromodiamine was isolated and further characterised by the preparation of its benzoyl and benzene-sulphonyl derivatives.

2. 3-Bromo-*p*-toluidine was successively nitrated and methylated, when a tertiary amine,—



was obtained, which on successive reduction and acylation gave rise to acyl derivatives identical with those produced by the foregoing method, and from which the same bromodiamine was produced on hydrolysis.

This base interacts with diazo-compounds only with difficulty; it gives an azo-dye on fabrics impregnated with diazotised primulin, but does not yield crystallisable azo-derivatives with the simpler diazonium salts.

*110. "The Action of Magnesium Methyl Iodide on Pinene Nitroschloride." By WILLIAM AUGUSTUS TILDEN and JOSEPH ARTHUR STOKES.

The Grignard reagent attacks partly the chlorine of the nitroschloride and partly the oxygen of the nitroso-group, substituting in each case an equivalent quantity of methyl. Two principal products are therefore obtained, namely, the oxime, $C_{10}H_{15}(CH_3):NOH$ (m. p. 193°), and a base, $C_{10}H_{16}ClN(CH_3)_2$ (m. p. 122°). The oxime possesses well-marked basic properties, and forms a crystallisable hydrochloride. The chlorine present in the base is not exchangeable for methyl by the further action of the reagent, but when treated with alcoholic potash it loses the elements of hydrogen chloride and produces an unsaturated base, $C_{10}H_{16}N(CH_3)_2$ (m. p. 112°), which is identical with dimethylpinyllamine. Benzoyl and methyl ethers of the oxime are described in the paper as well as the hydrochlorides and other salts of the saturated chloro-base, of the unsaturated base derived from it, and of dimethylpinyllamine prepared from pinyllamine.

111. "The Action of Hypobromous Acid on Piperazine," By FREDERICK DANIEL CHATTAWAY and WILLIAM HENRY LEWIS.

The N-dichloro-derivative of piperazine was described several years ago, but the corresponding bromine compound had not hitherto been prepared, owing probably to the circumstance that the action of hypobromous acid in excess on piperazine gives rise, not as usual to the substituted nitrogen bromide, but to an additive product of hypobromous acid and the base. The additive product, which is insoluble in water and chloroform, and rapidly decomposes on keeping, yields, however, diethylene dibromodiamine, $BrN(CH_2CH_2)_2NBr$, on treatment with an aqueous solution of the base. It crystallises from chloroform, in which it is easily soluble, in yellow, short, flattened prisms. On heating, it explodes with great violence at $79-80^\circ$ without previously melting.

112. "Racemisation Phenomena during the Hydrolysis of Optically Active Menthyl and Bornyl Esters by Alkali." By ALEXANDER MCKENZIE and HERBERT BRYAN THOMPSON.

A number of inactive acids were converted into their *l*-menthyl and *l*-bornyl esters respectively, and the latter then submitted to fractional hydrolysis by being heated first with an amount insufficient for complete hydrolysis, whilst the mixture of esters, which survived the attack of the alkali in the initial hydrolysis, was then hydrolysed by an excess of alkali. In several cases, optically active acids of the same sign were obtained as products, both of the initial and final hydrolysis. The results are indicated as follows:—

	Direction of rotation of the acid from the initial hydrolysis.	Direction of rotation of the acid from the final hydrolysis.
<i>l</i> -Menthyl <i>dl</i> -phenylethoxyacetate	—	—
<i>l</i> -Bornyl <i>dl</i> -phenylethoxyacetate	—	—
<i>l</i> -Bornyl <i>dl</i> -mandelate	—	Inactive
<i>l</i> -Bornyl <i>dl</i> -lactate	Inactive	—
<i>l</i> -Menthyl <i>dl</i> -lactate	+	—
<i>l</i> -Menthyl <i>dl</i> - α -ethoxypropionate .	—	+
<i>l</i> -Bornyl <i>dl</i> - α -ethoxypropionate . .	+	—

No resolution was effected with *l*-menthyl *dl*- α -hydroxybutyrate, *l*-bornyl *dl*- α -hydroxybutyrate, and *l*-menthyl *dl*- β -hydroxybutyrate respectively.

The racemising effect of alkali during the hydrolysis of the esters examined is discussed.

The fractional esterification of *i*-phenylethoxyacetic acid by *l*-borneol, the esterification of *l*-mandelic acid by *l*-borneol, the action of potassium hydroxide on *l*-malic acid, and the action of heat on the isomeric *l*-menthyl mandelates were investigated.

(To be continued).

NOTICES OF BOOKS.

The Sesquiterpenes. A Monograph by OSWALD SCHREINER. Milwaukee, Wis.: Pharmaceutical Review Publishing Company. 1904. Pp. 130.

THE study of the constituents of the so-called essential or volatile oils is one which, for a number of years, has engaged the attention of chemists, and has been attended with most interesting and important results. In fact, during the last quarter of a century no department of organic chemistry appears to have experienced a greater development, on both the scientific and the technical side, than that which comprises the great variety of substances contained in or related to the group of natural products commonly known as the essential oils. As examples of this activity there may be noted the researches on the constitution of camphor, and the recent endeavours for its synthetical production, as well as the large industries which have been created for the technical production of those substances which, being either original constituents of essential oils or derivatives of some definite constituent of them, are now so largely utilised in the art of perfumery.

In connection with other constituents of essential oils, particular attention has been devoted to the structure and classification of the hydrocarbons designated as *terpenes*. While, however, the terpenes proper, as represented by the formula $C_{10}H_{16}$, have been the subject of many extended and brilliant investigations, which, among other results, have afforded a rational and truly scientific basis for their characterisation, the large number of hydrocarbons having the molecular formula $C_{15}H_{24}$, designated as *sesquiterpenes*, have hitherto received comparatively little attention. The apparent neglect of this group of substances is attributable to the experimental difficulties connected with their investigation, but with the advance of knowledge there is reason to anticipate that, to some extent at least, these difficulties may also be overcome.

The recently published monograph by Dr. Schreiner is the outcome of studies pursued at the School of Pharmacy of the University of Wisconsin, in association with Professor Edward Kremers, who is well known for his contributions to the literature of the terpenes. It is an attempt to bring together the known facts relating to the sesquiterpenes, and on this basis to indicate the means by which their scientific classification may be effected and a further knowledge of them acquired. The subject matter of the work is divided into a General Part and a Special Part. In the former there are considered:—

- I. The position of the sesquiterpenes in the various systems of classification of the terpenes at large (C_5H_8)_x.
- II. The position of the sesquiterpenes in the modern rational system of classification of hydrocarbons.
- III. Classification and comparison of the better known sesquiterpenes and discussion of possible constitution and synthesis.
- IV. The occurrence of sesquiterpenes in the vegetable kingdom.

In the special part a number of sesquiterpenes to which specific names have already been given are considered in detail with respect to their sources and their physical and chemical characters, and these are followed by a number of other substances of this class obtained from various essential oils, but the characterisation of which is less complete.

The work has evidently been compiled with much care and the exercise of critical judgment. It is believed that it will be found exceedingly useful to those who are interested in this branch of chemistry, as it not only contains in a concise form a summary of existing knowledge concerning the sesquiterpenes, but is suggestive of lines of investigation that may still be profitably pursued.

The Follies of Science at the Court of Rudolph II. By HENRY CARRINGTON BOLTON. Milwaukee, Wis.: Pharmaceutical Review Publishing Company. 1904. Pp. 217.

THE late lamented author of this volume was well known for his valuable contributions to the bibliography of chemistry, as also for his many other writings on subjects pertaining to chemistry, folklore, travels, and general literature. The work to which he has given the above-mentioned title was apparently the last of his literary efforts, and it is an exceedingly entertaining narrative.

The suggestion for the production of this work appears to have been an oil painting by the Bohemian artist, Vaezlav Brozik, entitled "Rodolphe chez son Alchimiste," which is stated to hang in the building containing the Lennox Library in New York. A representation of this picture is given as a frontispiece to the work, and in the preface Dr. Bolton has graphically indicated its most interesting features. He states that in the text "an attempt has been made to describe the circumstances that make the picture historically accurate, and to give some account of the scientific atmosphere pervading the Court of Rudolph II., Emperor of Germany. Descriptions of persons, localities, and events are true to history, but the author has allowed himself the liberty of the artist in using the imagination in a few instances to lighten up the dull background of hard facts."

The contents of the work are comprised in nineteen chapters, and these are embellished with eighteen, mostly full page, illustrations. The various episodes in the history of alchemy, magic, and sorcery are described in a most interesting manner, and the information which they afford respecting the dogmas and superstitions of past centuries cannot fail to be appreciated by all students of modern science.

F. B. POWER.

Elements of Applied Microscopy. By CHARLES EDWARD AMORY WINSLOW. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1905.

THE exact position of this text-book among others dealing with various branches of microscopy is not easy to define. The limitations of space preclude the possibility of its providing anything like an adequate presentment even of the elements of the science of the application of the microscope to practical problems occurring during the examination of foods and drugs, paper manufacture, and the study of medicine, though the book touches upon all these subjects. At the same time, although the treatment is in all cases exceedingly elementary and even sketchy in places, there is something to be said for the author's opinion that the volume is the "outgrowth of a pedagogic need." The most useful portions appear to be undoubtedly those in which directions are given for the manipulation of the microscope and the preparation and mounting of objects, and as regards practical applications it would no doubt be found very difficult, if not impossible, to give any course which would be less sketchy than that to be found here without greatly enlarging the book.

Letters Touching Unrest, Cause and Remedy. By WILLIAM M. BABBOTT. New York: William M. Babbott. 1904.

THAT the importance of sociological questions is very great and constantly growing no one will deny, but at the same time it is open to doubt whether the publication of literature of this kind can do much towards solving the problems with which humanity is so constantly confronted in modern times. The magnitude of the questions involved, and the amelioration of the lot of mankind which would result if they were satisfactorily settled, seem to demand that at least careful attention should be paid to any honest attempt to discuss them fully and fairly, and for that reason possibly the work will find readers. But it is too much to expect that they will be satisfied that

mankind would be uplifted if the author had the direction of public affairs. He shows considerable power of invective when discussing the iniquities of the modern Captains of Industry, and gives graphic accounts of the commercial corruption which rules the world; he does not scruple to speak his mind and criticise in regions in which we may be allowed to doubt whether he is well qualified to judge, as, for instance, in his tirade against the farming system of Sir John Lawes among others. But the book may be searched through in vain to discover any practical suggestions to remedy the state of affairs he bewails. Moreover, the want of coherence, of literary style and method in these letters unavoidably prejudices the reader against them, and in reading the later chapters, which, according to the author, are not intended "by any means solely for self aggrandisement," he is induced to wonder whether they will serve any better and loftier purpose half so well.

Elettricità e Materia. ("Electricity and Matter"). By Dr. J. J. THOMSON. Translated by Dr. G. FAE. Milan: Ulrico Hoepli. 1905.

THE lectures which this book contains were delivered before Yale University in May, 1903, and deal with modern developments of electricity. When given by the distinguished professor they were heard with great interest, and this translation of them into Italian will no doubt be given a favourable reception by physicists of that nationality. The translator has contributed an interesting preface, giving a brief summary of the important points treated of, and has also made considerable additions to the text, especially in the chapter on radio-activity, to which an appendix is provided, briefly describing recent important publications.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxi., No. 20, May 15, 1905.

Permeability of Glass Vessels.—M. Berthelot.—The author makes a series of experiments on the permeability of glass vessels to gases at temperatures approaching their softening-point, and finds that glass walls, in the same way as quartz walls, are permeable to gases when maintained almost at softening temperature, an exchange taking place between the gases contained in the vessel and atmospheric gases.

Menthones and Menthols obtained by the Reduction of Pulegone by the Catalytic Action of Reduced Nickel.—A. Haller and C. Martine.—The authors use MM. Sabatier and Senderens' method of hydrogenation of pulegone, in order to avoid the formation of resinous products. The result is the formation of one or several saturated ketones corresponding to different menthones or a mixture of menthols.

Constitution, Saccharification and Retrogradation of Starch.—L. Maquenne and Eug. Roux.—The authors find that natural starch is a mixture of two substances, essentially different. The chief component is partially soluble in water at 100° and absolutely soluble in superheated water, and is identical with the material already known under the name of amylo-cellulose. In the soluble state it is turned blue by iodine, and is transformed entirely into maltose under the action of malt at a low temperature. In the solid state it is unaltered by both reagents. The second component, present in smaller proportion, is a

mucilaginous body, which the authors propose to call amylopectine. It is not coloured by iodine even when in the liquid state, and dissolves in malt extract without formation of sugar. It is the presence of this substance in natural starch which causes the latter to gelatinise under the action of boiling water or alkalis. Artificial starch differs from natural starch only by the absence of amylopectine.

Tribo-luminescence of Metallic Compounds.—D. Gernez.—The author finds about a hundred tribo-luminescent substances, of which seventy-four are purely mineral, the twenty-six others being metallic salts of the organic acids. Thus it is shown that tribo-luminescence is not a special property of the organic acids, as was hitherto believed. Doubtless, with a more sensitive instrument than the human eye, a much greater number of compounds would manifest this property.

Properties of certain Anhydrous Chlorides of the Rare Earths.—Camille Matignon.—In a previous paper the author gave an account of a preparation of the pure anhydrous chlorides of the rare earths. He now examines the properties of these chlorides, and finds certain of their physical constants, which are given in the following table:—

	La.	Pr.	Nd.	Sm.
Atomic mass	138.6	140.5	143.6	150
Density	3.947	4.017	4.195	4.465
Fusion-point	907°	818°	785°	686°
Heat of solution (cals.)	31.3	33.5	35.4	37.4
Heat of formation from the oxide and hydrochloric acid gas (cals.)	80.3	73.9	71.6	64.2

Reaction for Rhodium.—E. P. Alvarez.—Already inserted.

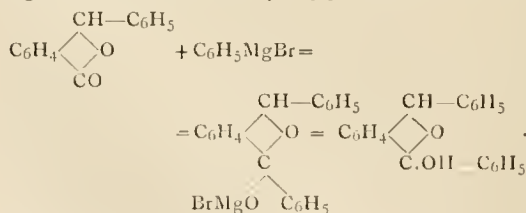
Action of Ammonium Metals on Alcohols. General Method for the Preparation of Alcoholates.—E. Chablay.—The author succeeds in preparing alcoholates at a low temperature. This preparation consists in dissolving separately the alkaline metal and alcohol in liquid ammonia, and then mixing the two ammoniacal solutions. The method of operation is the same for all alcohols. The results show that the reaction of the ammonium metal is really that of the alkaline metal itself, and can be represented by the equation $R.CH_2.OH + NH_3Na = R.CH_2.ONa + NH_3 + H$.

Propionylcarbinol and its Derivatives.—André Kling.—The reactions which the author describes show that propionylcarbinol is comparable with its inferior homologue, acetol, and that in aqueous solution it takes

the form of an acid of constitution $C_2H_5O \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} OH \\ O \end{smallmatrix} CH_2$.

This acid is less energetic than that given by acetol, since it is unable to combine with methyl alcohol. However, it is apparently more stable. Anhydrous propionylcarbinol appears to be a mixture of two tautomeric forms. The ether salts of propionylcarbinol only exist under the ketonic form $C_2H_5COCH_2-R$.

Derivatives of Benzodihydrofurfurane.—A. Guyot and J. Catel.—The authors investigate the properties and reactions of the diphenyloxy- $\alpha\alpha'$ -benzo- $\beta\beta'$ -dihydro- $\alpha\alpha'$ -furfurane, which is produced by the action of phenylmagnesium bromide on monophenylphthalide,—



This latter substance very easily loses a molecule of water by simple desiccation.

MISCELLANEOUS.

Messrs. Armbricht, Nelson, and Co. have just issued a list of Rare Elements they are now in a position to supply. This list gives not only the prices, but the symbols, atomic weights, specific gravity, discoverer, principal source, melting-point, &c., of these elements, and the form in which they are sold, such as the oxide, fluoride, oxalate, &c. Forty elements are comprised in this list, and special attention is drawn to metallic calcium in bars weighing from 4 ozs. to 16 ozs. at 1s. 6d. per oz. It is interesting to note that in a recent list metallic calcium is quoted at 6s. 1d. for 15 grains, or about 19g per oz.

Tollens' Gas Measuring and Absorption Burette.—This new burette consists of a glass tube with a bulb and stopcock, holding 100 c.c. between the gauge marks, and is fitted with a piston. By means of this apparatus it is possible to make a determination of carbonic acid in furnace gas in about two minutes, and another minute would be required to determine the presence of oxygen. This saving of time is due to the use of a piston instead of the slow-working levelling bottle. Another advantage is that no water comes into contact with the gas before the first readings are taken; thus errors due to absorption by water are avoided. The manipulation is extremely simple, the piston and a stopcock being the only moving parts. The apparatus is securely packed in a wooden box, with the necessary reagents, and can be obtained from Messrs. A. Gallenkamp and Co., Ltd.

Action of Ammonium Metals on the Halogen Derivatives of Methane.—E. Chablay.—The hydrogen carbides, with the single exception of acetylene, have only a very slow or else no action at all on the alkaline ammoniums; the author investigates the action of these latter compounds on the chloro- or iodo-derivatives of the carbides. His first experiments are made on methane derivatives.—*Comptes Rendus*, cxl., No. 19.

Perstannic Acid and Perstannates.—S. Tanatar.—If stannic acid, precipitated from tin chloride solution by means of soda, and well washed, is rubbed up with twice as much 30 per cent hydrogen peroxide as is theoretically necessary to convert it into perstannic acid, and the mass is then dried at 70° on the water-bath till it becomes pasty and begins to crack, after a few days' drying in the desiccator it is converted into a white amorphous powder, with the formula $HSnO_3 + 2H_2O$. It loses water and oxygen slowly in the desiccator, and is only very slightly soluble in water, which partially decomposes it into hydrogen peroxide and stannic acid. After being dried at 100° its composition is represented by the formula $H_2Sn_2O_7 + 3H_2O$. Potassium perstannate is prepared by cooling a mixture of a solution of potassium stannate and 30 per cent hydrogen peroxide with ice-water, and precipitating with alcohol. After washing with alcohol and ether, and drying in the desiccator, a white amorphous powder is obtained, which loses oxygen and water on ignition. The aqueous solution of the salt is alkaline, and contains some free hydrogen peroxide. Continued drying converts it into $K_2Sn_2O_7 + 3H_2O$. Sodium perstannate is prepared similarly, but being almost insoluble in water it is precipitated more readily. The solution of potassium perstannate gives precipitates with Ba, Sr, Mg, Zn, Ni, Co, and Pt salts; these precipitates are mixtures of the hydroxides of the metals with perstannates. With the exception of the barium and strontium perstannate they are decomposed by water, oxygen being evolved.—*Berichte*, xxxviii., No. 5.

Preparation and Properties of Manganese Borides.—E. Wedekind.—Under suitable conditions a reaction occurs between molten manganese and amorphous boron, when a crystalline regulus is obtained, containing a compound of the metal and boron. This compound yields boron hydride on treatment with warm water. Its com-

position is not quite constant, the amount of manganese present varying up to 82.3 per cent. On heating a current of chlorine at a dark red heat over the raw product, the unchanged reagents are converted into chlorides, while a black crystalline substance remains behind, which is very stable towards chlorine, but slowly decomposes with water. The amount of manganese present in it corresponds to the formula MnB_2 . With fused potash this boride is converted into manganate and borate, and it evolves boron hydride with dilute acids. In absence of moisture it is very stable, and may even be heated in air. The boride prepared from manganoso-manganic oxide and boron in the electric furnace has the formula MnB , and appears to be formed according to the equation $3Mn_3O_4 + 17B = 9MnB + 4B_2O_3$. It is very similar to the preceding in appearance and behaviour, but on heating on platinum-foil it melts and decomposes.—*Berichte*, xxxviii., No. 5.

MEETINGS FOR THE WEEK.

WEDNESDAY, 21st.—Microscopical, 8. "Theories of Microscopical Vision" (II.), by A. E. Conrady. "The Tubercle Bacillus," by Edward M. Nelson.



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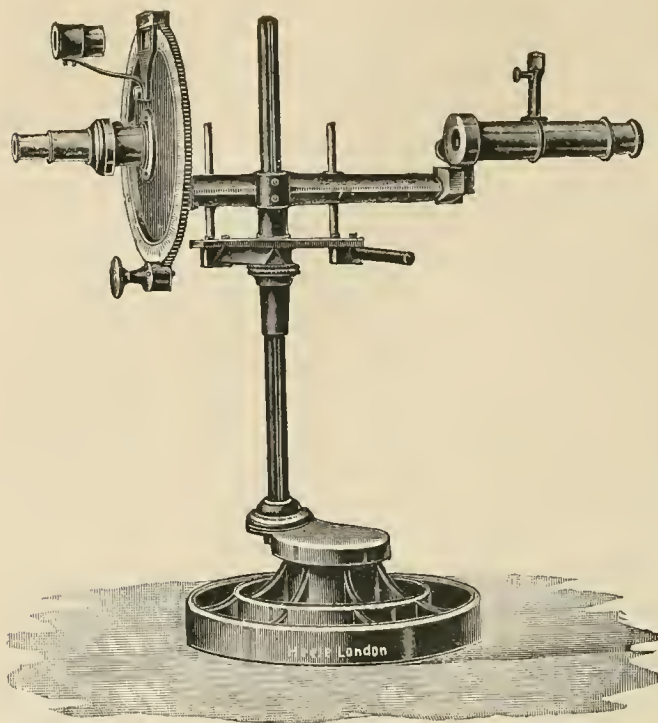
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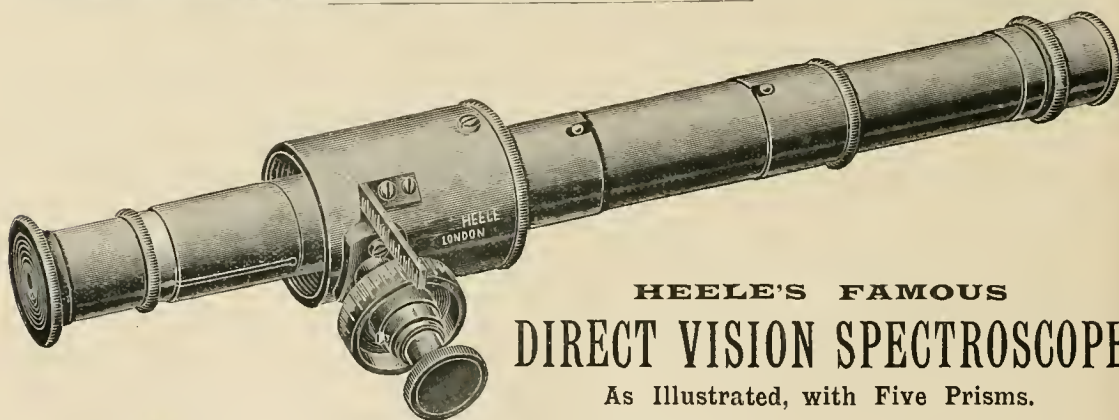
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VOL. XCI., No. 2378.

THE DIRECT SYNTHESIS OF AMMONIA.*

By EDGAR PHILIP PERMAN, D.Sc.,
Assistant Professor of Chemistry at University College, Cardiff.

It was shown in a recent Paper on "The Decomposition of Ammonia by Heat" (*Proc. Roy. Soc.*, 1904, vol. lxxiv., p. 110) that ammonia is decomposed almost (if not quite) completely when heated in a porcelain vessel at about 800° to 1100°, and that there is no sign of equilibrium between the ammonia and its decomposition products at any of the temperatures employed, 677° to 1111°.

In order to discover if there is any such state of equilibrium, it was thought better to attempt to reach that state by synthesising ammonia instead of decomposing it, as the testing for and estimation of the ammonia could then be carried out with much greater accuracy.

Preparation of the Mixed Gases.—In the first series of experiments, the mixture of nitrogen and hydrogen was made by passing ammonia gas, from a strong aqueous solution, through a red-hot iron tube heated in a gas furnace, and the resulting gases were collected in a large gasholder and stored over dilute sulphuric acid. It may be objected to this method of preparation that carbon monoxide, hydrogen, and other gases would percolate through the iron, and contaminate the product obtained. In order to test this point, a careful analysis of the gases was made, with the result that no carbon monoxide could be detected by the blood test; no carbon dioxide was found after exploding the gases with oxygen; and the ratio of nitrogen to hydrogen was found to be correct. The mixture of gases made by this method will be referred to as "Mixed Gases I."

It was thought, nevertheless, that traces of foreign gases might have escaped detection, and might possibly have influenced the results. Consequently a second series of experiments was carried out with a mixture of nitrogen and hydrogen made in an entirely different way. Nitrogen gas was made by heating gently a solution of equivalent quantities of ammonium chloride and sodium nitrite, and hydrogen was prepared from a concentrated potash solution heated with metallic aluminium, the gas being passed through two Drechsel flasks containing potassium permanganate solution.

Each gas was stored in a gasholder, and a mixture of the two was then made, in the proportion of 1 volume nitrogen to 3 volumes hydrogen, in a third gasholder. The volume of gases was measured by the volume of water drawn off, due regard being paid to the "head" of water. This mixture will be called "Mixed Gases II."

Attempted Synthesis by Heat (Mixed Gases I. and II. separately).—The mixture was proved to be free from ammonia by testing with Nessler's solution. It was then passed through a hard glass tube heated in a combustion furnace. Glass was chosen as likely to have no chemical action on ammonia or its constituents. The temperature was varied from about 600° to 1000° C. The resulting gases were bubbled through dilute hydrochloric acid solution; this was afterwards made alkaline with potash, and Nessler's solution added. The result was that *no ammonia could be detected*, whatever the temperature or state of gases as to moisture.

In some experiments the mixture was freed from traces of oxygen by bubbling through alkaline pyrogallate solution, and then dried by strong sulphuric acid; in other experiments these precautions were omitted, but the result was always the same, and was obtained many times.

The experiment was varied by filling a porcelain globe with nitrogen and hydrogen (Mixed Gases I.), and heating it in a furnace to a bright red heat for about one and a-half hours. The gases were then tested for ammonia in the usual way, but not a trace was found. We may conclude, therefore, from these experiments, that ammonia cannot be synthesised from nitrogen and hydrogen by heating in vessels of glass or porcelain, or that, if it is formed, it is not in sufficient quantity to be detected by Nessler's solution.

Synthesis by Heat in the presence of Iron. (Mixed Gases I.)—Some of the mixed gases were then passed through an iron tube heated to redness, or in some cases a glass tube containing iron nails, and it was found that, when moisture was present, traces of ammonia were formed; if however, care was taken to exclude moisture by passing the gases through alkaline pyrogallate solution and sulphuric acid, and reducing any iron oxide, then no ammonia could be detected. This result was obtained also by Ramsay and Young (*Journ. Chem. Soc.*, 1884, vol. xlv., p. 88).

In order to form an idea of the amount of ammonia produced, known volumes of the mixed gases were passed through a hard glass tube packed with "French nails," and the ammonia was estimated by Nessler's solution, as in the method used in water analysis. The following results obtained:—

Vol. of mixed gases.	Approximate rate.	Ammonia.
C.c.	Litres per hour.	M.grm.
500	10	0.03
500	10	0.06
250	3	0.08
250	3	0.10

No ammonia could be detected in any case unless the iron was at a bright red heat, about 800° to 900°. With Mixed Gases II.:—

Time.	Vol. of mixed gases.	Ammonia.
"	C.c.	M.grm.
8 20	250	0.20
2 45	250	0.20
0 42	250	0.17

It will be noticed that the maximum amount of ammonia was formed when the gases were passed at the middle rate, indicating that the mixture had come into equilibrium. More than twice as much ammonia per litre of mixed gases was formed in this series as in the first, and it appeared to be formed at a lower temperature. Moreover, when the gases were carefully dried by sulphuric acid, traces of ammonia were still found. Whether this difference was due to greater purity of the gases or to any other variation in the conditions (*e.g.* the new French nails) I am unable to say.

My attention has been called to a paper by Haber and van Oordt (*Zeit. für Anorg. Chemie*, 1905, vol. xliii., p. 111) in which some very similar experiments are described. The proportion of ammonia formed in the experiments of these investigators was about 0.2 to 1000 possible (if completely converted), which is considerably less than obtained by me, but the temperature and other conditions were different in the two cases.

Haber and van Oordt have attempted to find the dissociation constant at different temperatures, but it appears to me that the available data are entirely insufficient for the purpose. Moreover, the part played by the iron is not yet completely understood.

My experiments show that the quantity of ammonia formed depends on the amount of moisture present, but Haber and van Oordt appear to have overlooked this point, and say simply that their gases were dry.

Synthesis by Heat in the presence of other Substances.—Similar experiments were made with a number of other metals. Copper, zinc, nickel, cobalt, palladium, aluminium, and magnesium, all gave traces of ammonia, but usually

* A Paper read before the Royal Society, March 30, 1905.

less than iron. Platinum sponge yielded traces, whilst platinised asbestos and platinum-foil produced very minute and scarcely perceptible quantities. Zinc and copper in contact gave no more than when present separately. In all these cases, which were made with "Mixed Gases I.," no attempt was made to exclude moisture.

Effect of Large Surface (Mixed Gases I.)—The following substances were selected in order to test the influence (if any) of large surfaces, on the synthetical formation of ammonia:—Pipe stems, pumice, broken porcelain, asbestos. A hard glass tube was packed with the substance, and the experiment conducted in the usual way. As the result, traces of ammonia were found in each case, except with the porcelain. All these substances, except the porcelain, contained a notable quantity of iron, and I believe that it is owing to its presence that the ammonia was formed. The porcelain was from a broken globe (see former paper, *loc. cit.*). The pipe-stems altered in colour, under the influence of the gases, from a yellowish tint to a dull grey, which I ascribe to the reduction of the iron present. Although my conclusion may be questioned, I believe that (in this case) the extent of surface has no effect, unless the substance with which the gases are in contact reacts chemically with them.

Synthesis by Explosion.—It was noticed that if an explosion of the mixed gases and air took place in the hard glass tube, traces of ammonia were formed, and the effect was further investigated by exploding the gases with oxygen in a eudiometer and testing the resulting gases for ammonia. The following are the results:—

Mixed gases. C.c.	Oxygen. C.c.	Result.
10.5	2	Trace of ammonia.
15	5.2	Ditto (but less).
16	3.5	Ditto.
16.3	3.4	Ditto.
16	9	Ditto (but less).

It will be seen that the quantity of ammonia formed diminishes if the oxygen is in excess. The quantities were very small, but nevertheless considerably greater, in proportion to the volume of gases taken, than those produced by the action of iron. Similar effects have been noticed by other investigators (see "Watts' Dictionary," 1st Ed., Art. "Ammonia").

Synthesis by Sparking.—It is well known that ammonia can be synthesised in small quantities with the aid of high potential electric discharges, and I have now attempted to bring the gases into a state of equilibrium during sparking, *i.e.*, into such a state that the rate of decomposition is equal to the rate of formation of the ammonia, and to reach that condition from each direction.

Mixed Gases I.—The experiments were carried out in a glass bulb of about 250 c.c. capacity, provided with two tubes and stopcocks, and with platinum wires for sparking, the sparking distance being about 25 m.m.

The bulb was placed in a thermostat and maintained at a temperature of 40° C., it was filled with the mixed gases, and the platinum wires connected with the terminals of an induction coil capable of giving an 8-inch spark.

After the sparking the gases were aspirated into dilute hydrochloric acid solution and nesslerised. The various results are put together in the following tables:—

Pressure	Time of sparking. Mins.	Ammonia formed. M.grms.	Remarks.
Atmospheric	5	0.02	Moist gases.
"	15	0.06	"
"	15	0.02	Very thin spark.
"	5	0.02	Gases dried by H ₂ SO ₄ .
"	10	0.03	
"	15	0.06	
"	20	0.07	
"	30	0.10	
"	45	0.10	"
2 atmospheres	60	0.19	"
"	30	0.19	"

From these results it will be seen that:—

1. Under atmospheric pressure equilibrium (as before defined) was reached when 0.1 m.grm. ammonia had been formed.

2. Under a pressure of two atmospheres equilibrium was reached when 0.19 m.grm. was present.

3. The amount of ammonia formed depends on the quantity of electricity passing, thus a very thin spark produced only one-third as much ammonia as a "fat" spark in the same time.

Decomposition of Ammonia by Sparking.—Attempts were made to reach the same equilibrium points by starting from the opposite end of the reaction. It was found to require long sparking before equilibrium was nearly reached. The following are the results:—

Pressure.	Time of sparking. Hours.	Ammonia remaining. M.grms.
Atmospheric, allowed to blow off every few minutes	2.5	0.13
Atmospheric, rising to two atmos. at end.	5	4.2
Two atmos., commencing with a mixture of N and H (1:3), and 2 per cent NH ₃	2	0.56
Two atmos., commencing with a mixture of N and H (1:3), and 1 per cent NH ₃	2.5	0.32

At atmospheric pressure decomposition was rapid, and the equilibrium point was very nearly reached, synthesis giving 0.10 m.grm. and analysis 0.13 m.grm. When the volume was kept constant, decomposition was very slow, and the point of equilibrium was approached only by starting a long distance from the beginning of the decomposition. Starting with a mixture containing 1 per cent of ammonia, after two and a-half hours' sparking, 0.32 m.grm. ammonia remained instead of 0.19 m.grm. by the synthetical method.

Mixed Gases II.—In this series the length of the spark was 11 m.m., and the capacity of the globe 262 c.c. At the conclusion of the experiment the gases were pumped out through dilute acid. The temperature was 39.8° C.

Time. Mins.	In primary coil.		Ammonia. M.grm.
	Current. Ampères.	Voltage.	
15	2	4	0.08
30	2	4	0.30
15	1.5	4	0.25
30	5.5	4	0.44
45	5.5	4	0.37
22.5	5.5	4	0.41
15	2.75	2	0.07

Decomposition of ammonia by sparking.

68	5.5	4	0.41
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From these results it is seen that:—

1. Equilibrium was reached in about twenty-two minutes, the gases then containing 0.41 m.grm. ammonia. On sparking ammonia at atmospheric pressure exactly the same point of equilibrium was reached.

2. More ammonia is formed than in the first series, owing to the shorter spark; also the rate of decomposition and the rate of formation are quicker.

3. Other conditions remaining the same, the amount of ammonia formed is roughly proportional to the current strength.

4. If the current strength remains the same, the quantity of ammonia formed is much influenced by the voltage. (It must be remembered that the electrical measurements here mentioned are those of the primary coil).

Since writing the above, I have discovered that Berthelot carried out experiments of a somewhat similar nature. He found that, starting either with ammonia or with nitrogen

and hydrogen, sparking left finally a minute quantity of ammonia which was "of the same order" in the two cases ("Mécanique Chimique," 1879, vol. ii., p. 358). Using the silent discharge, he obtained the same point of equilibrium, starting from either direction, viz., a mixture containing 3 per cent ammonia. Reference should be made also to the work of Hemptinne, who has investigated the synthesis of ammonia under various conditions (*Bull. Acad. Roy. Belgique*, 1902, p. 28).

Summary.

1. So far as can be shown by one of the most delicate tests known to chemists, ammonia cannot be synthesised by heat (except under special conditions specified below). The decomposition of ammonia by heat may therefore be regarded as an irreversible reaction.

2. Ammonia may be synthesised in small quantities from its constituent elements (a) by heating with many of the metals; (b) by exploding with oxygen; (c) by sparking. These are reversible reactions.

3. It would appear that the synthesis of ammonia is effected only when the gases are ionised; the ionisation would be brought about by sparking, or by the high temperature of an explosion of hydrogen and oxygen. The immediate decomposition of the ammonia formed would be prevented by its sudden cooling. The metals in the presence of moisture also produce "nascent" or ionised hydrogen.

4. It does not appear that nitrides of the metals form an intermediate stage in the formation of ammonia, for it was found that metals readily forming nitrides, e.g., magnesium, did not produce more ammonia than the others.

5. There is a close analogy between ozone and ammonia with regard to their synthesis and decomposition; both are formed by sparking, and both are completely decomposed by heat.

In conclusion, I wish to express my thanks to Mr. G. A. S. Atkinson, B.Sc., and to Mr. J. H. Davies, B.Sc., for valuable assistance rendered during the earlier and later portions of the work respectively.

ELECTRICALLY HEATED CARBON TUBE FURNACES.*

PART I.

By R. S. HUTTON, M.Sc., and W. H. PATTERSON, B.Sc.

(Concluded from p. 274).

Agglomerated Carbon Tube Furnaces.—Where a considerable amount of work has to be done, the time necessary for boring and turning graphite tubes, which on account of the thin walls are always mechanically weak, is obviously a disadvantage. For most of our experimental work, therefore, we have made use of agglomerated carbon tubes, which can readily be obtained of almost any desired size from the several manufacturers of arc carbons. The amorphous carbon, being very hard, cannot be machined in the simple manner which is possible with graphite, and even grinding with carborundum wheels is a somewhat laborious operation; it was therefore decided to adopt a quite different method of making the electrical connections.

The construction finally adopted has proved itself so excellent in actual use that we believe it to be capable of wide application in electric furnace work, and have already adopted it for several types of resistance core furnaces.

The ends of the carbon tube, which may with advantage be somewhat roughened by filing, are electro-coppered, and then soft-soldered to thick copper tubes just large enough to slip over them. The copper tube is provided for a short distance with a brazed-on water jacket, which effectively cools the joint and protects it, even when very high current-density is necessary; at the further end of the copper tube a copper clamp connected with flexible cables leads in the current. By soft-soldering the carbon to copper tubes with brazed water jackets, it is always possible to easily replace the carbon without any fear of

injuring the joints of the water jacket. The length over which the soldered joint has to be made obviously depends on the size of carbon tube and the strength of current to be sent through it, but with this water cooling the necessary surface of contact is surprisingly small.*

For the earlier experiments, carbon tubes 30 c.m. long, 15 m.m. internal, and 20 m.m. external diameter were employed; these were jacketed as before with carborundum, which was generally kept in place with an external asbestos tube and asbestos washers fitting tightly up against the ends of the water jackets.

A similar construction has been used with much larger tubes) 60 c.m. long, 67 m.m. internal, and 82 m.m. external diameter), as shown in Fig. 2. The horizontally placed tube is capable of taking a number of small crucibles containing the material to be heated, but it is hoped to use these and still wider tubes in a vertical position, in which case a useful means of heating larger crucibles will be available. With these large tubes it is advisable to use some sort of diaphragm near the ends to prevent the radiated heat from burning the surface of the rubber or cork stoppers, which, as the copper is effectively cooled by the water jacket, can serve to attach the gas inlet and outlet extensions; with the small tubes there is no need to take this precaution.

During the past few months tube furnaces of this simple type have been in constant use, and have been found to work with satisfaction. The rapidity with which a very high temperature can be obtained, and the regulation of that temperature by simple variation in the strength of the current render their use very convenient. On the other hand, by starting with a relatively small current it is possible to raise the temperature as slowly as desired, and thus not to exceed any required maximum. Without the more trustworthy data, which it is hoped to obtain by the use of the optical pyrometer, it does not seem advisable to hazard any estimate of the highest temperatures which can be reached with this method of heating.

Owing to the porosity of the carbon tubes at high temperatures, it is difficult, even with a fairly rapid current of hydrogen, to keep the gas in contact with the heated material free from carbon monoxide. Since this was highly desirable in some of the experiments we have been carrying out, a modified form of construction was adopted for this special case. In the first modification the carbon tube was surrounded with a water-cooled, gas-tight, metal jacket through which hydrogen was passed, but with this arrangement the convection currents in the external gas carry off an enormous amount of heat, and a very high current density is required to reach even moderately high temperatures. On the other hand, when the carborundum-jacketed tube is, as a whole, surrounded with the gas jacket, the gas in the inner tube still contains 1 or 2 per cent of carbon monoxide, which is probably due to the carborundum containing a small amount of unreduced silica. The arrangement finally adopted (see Fig. 3) has worked well, and is, moreover, considerably more efficient than when a bare carbon tube is surrounded with a large gas enclosure. The central carbon tube (30 c.m. long, 15 m.m. internal, 20 m.m. external diameter) forms the heating tube proper, and alone carries the current; it is surrounded by another carbon tube (3.0 c.m. internal diameter), which is jacketed with carborundum as a heat-insulator. Both carbon tubes are provided with water-cooled copper-tube extensions. Hydrogen is passed through the space between the two carbon tubes, as also through the inner carbon tube, and in this way it is easy to keep the gas in contact with the heated material almost absolutely free from oxygen compounds.

For a large number of purposes these precautions are

* An experiment was carried out to test the perfection of these joints. One of the smaller tubes was surrounded with calcined magnesite, and heated with 300 amperes until the tube was practically completely destroyed. After cooling, the core was examined, and found to have burnt away to a mere shell right up to the copper; the joint, however, was still undamaged, and not even a drop of solder had melted out of it.

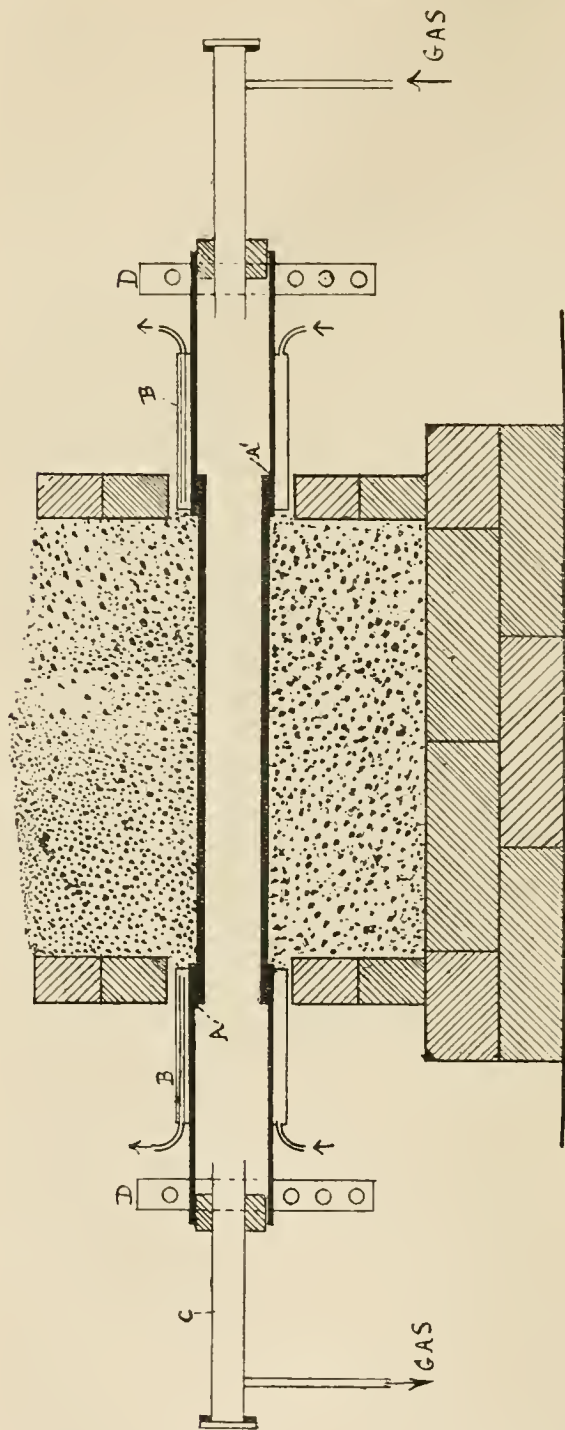


FIG. 2.—SIMPLE CONSTRUCTION OF AGGLOMERATED CARBON TUBE FURNACE.

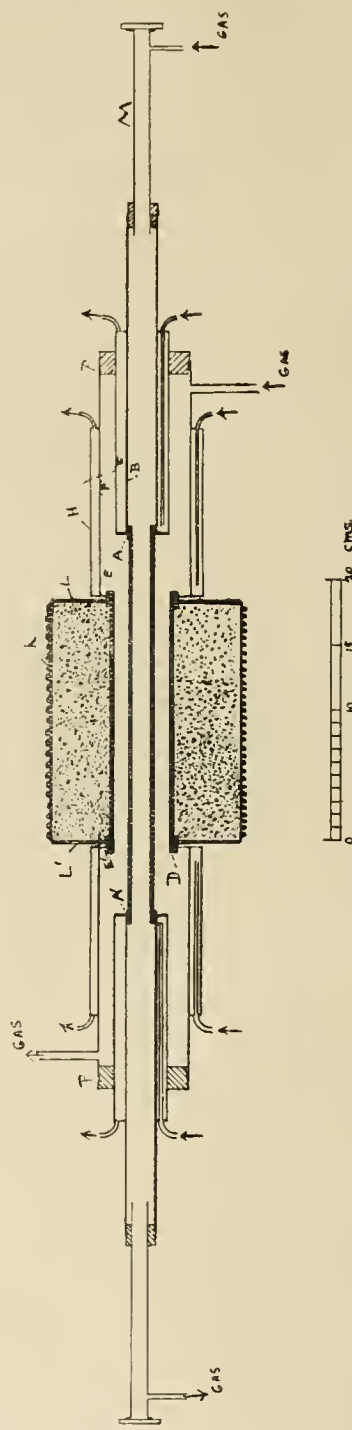


FIG. 3.—SPECIAL TUBE FURNACE FOR EXPERIMENTS IN PURE GAS ATMOSPHERE.

(FIG. 2.—The ends of the carbon are coppered and soldered at A and A' to copper tube extensions provided for a short distance with water jackets, B, which keep the joint cool. The current is led in by copper clamps, D. Glass tubes, C, are connected to the ends of the copper tubes by rubber stoppers, and serve for the passage of gas and for observation of the progress of the experiment. Smaller tubes of essentially the same construction have also been much used).

(FIG. 3.—The central carbon tube, A A', carries the current, and is the heating tube proper; it is provided with copper

water-cooled extensions, B C, to which the current is led by clamps not shown. To ensure the purity of the gas in the tube A A', it is surrounded by a concentric carbon tube, E E', which is also provided with copper water-cooled extensions, F H, a gas-tight joint between the two tubes being made by the rubber stoppers P. The outer carbon tube is jacketed with a granular heat-insulator to prevent, as far as possible, the radiation of heat. This granular material is held in place by asbestos washers, L, and an asbestos tube, K. Glass extensions, M, serve—as in Fig. 2—for the passage of gas through the heated tube, and for observing the progress of the experiment).

quite unnecessary, and the simpler form of construction is all that is required; we have therefore ourselves confined the use of this furnace to some experiments in which it was desired to study the action of carbon on some metals without the intervention of carbon monoxide.

In all our experiments we have had to use continuous current, although obviously low-tension alternating current obtained by the use of a transformer would be much more convenient, particularly with the large-sized tubes.

In many laboratories the high currents required will certainly be a hindrance to the employment of such carbon tube furnaces, but in these cases it may be an advantage to increase the resistance of the tube by some such method as that proposed by E. Ruhstrat and E. W. Grimmer (Brit. Pat. 24,472, Nov. 18, 1903), who cut a spiral on the carbon tube, and thus form a more or less narrow helix, which can be made to take quite small currents at correspondingly higher voltage.

In view of the prospect of shortly having fairly trustworthy data as to the temperature variations during the experiments, it is thought advisable to retain for a later paper full details as to the current and voltage readings at different temperatures. The following are only approximate values, which will, however, suffice to indicate the conditions under which the experiments have been carried out. The readings are those observed when the temperature indicated had been reached, and since the resistance obviously decreases as the temperature rises they must not be taken to indicate mean values.

Type of furnace.	Jacketing material.	Observations.
Graphite; 28 c.m. long, 2.0 external, 1.5 internal diameter.	Carborundum.	295 amps. at 8.2 volts melts nickel in 26 mins.; 320 amps. at 9.6 volts melts nickel in 13 mins.; platinum in 16½ mins.
Agglomerated carbon; 27 c.m. long, 2 c.m. external, 1.5 c.m. internal diameter.	Carborundum.	140 amps. at 7.7 volts melts nickel in 19 mins.; platinum in 28 mins.
Agglomerated carbon; 27 c.m. long, 2 c.m. external, 1.5 c.m. internal diameter.	None; bare tube surrounded with hydrogen.	235 amps. at 16.4 volts required to melt nickel (5½ mins.).
Agglomerated carbon; dimensions, &c., as Fig. 3.	Carborundum outside outer carbon tube.	200 amps. at 21 volts melt nickel in 3 mins.; current increased to 240 amps. at 25 volts, melting platinum, in further 2½ mins.
Agglomerated carbon tube; 60 c.m. long, 8.2 c.m. external, 6.7 c.m. internal (as Fig. 2).	Carborundum.	600 amps. at 8.6 volts give 1200° C. in 30 mins. (temp. still rising 7° per min.); 850 amps. at 13.0 volts melt nickel in 12 mins.; platinum in further 8½ mins.; later much hotter, and takes 860 amps. at 11.1 volts.

Important differences manifest themselves according to the type of furnace construction adopted. With a bare tube surrounded with a gas jacket, a given current very soon brings the carbon up to a temperature which remains more or less constant, or at the most only continues to rise very slowly; on the other hand, with carbons closely jacketed with a granular material, which is a good insulator, the temperature continues to rise for a very long time, and in this way, with a much smaller current and expenditure of power than is required in the previous case, a high temperature can be *built up*. As the temperature rises, however, the jacketing material becomes an electrical conductor, and even pure oxides at or near their fusing-point become good conductors, and by carrying some of the current tends to limit the temperature attainable. Further experiments are required to show the relative behaviour of different materials in this respect.

One of the great advantages of such furnaces over those in which the heat is obtained from an electric arc or a granular resistance material lies in the fact that the temperature can be much more easily regulated and kept constant.

There is such a vast amount of physical and chemical high-temperature work which can only be carried out when the heating is under perfect control that we feel confident in finding numerous applications for these carbon tube furnaces.

ON A NEW TYPE OF ELECTRIC FURNACE, WITH A RE-DETERMINATION OF THE MELTING-POINT OF PLATINUM.*

By J. A. HARKER, D.Sc., Joule Scholar of the Royal Society,
Assistant at the National Physical Laboratory, Teddington.

(Concluded from p. 275).

XIII. Use of the New Type of Furnace in Various Physical Investigations.

A FEW further words may be said regarding the furnaces, one type of which is here described. Preparations are now being made for building them on a much larger scale, and it is hoped to publish shortly a further account of their construction and uses. In addition to their use for work such as is here detailed, the type of furnace appears to be capable of numerous applications, both scientific and technical.

Of the scientific applications might be mentioned its use in the determination, at steady high temperatures in the absence of noxious gases, of the general physical properties of bodies, such as their coefficient of expansion, density, and specific heat in both liquid and solid states, and also vapour density and dissociation. A horizontal form could easily be arranged for softening and annealing of long lengths of continuous wires, particularly such as cannot be directly heated electrically by current.

It is quite easy to arrange such a furnace to work *in vacuo*, and in this form it might be of use in many chemical investigations. In the preparation of metals like silver for such work as the determination of its electrochemical equivalent, where the highest possible purity of the product is desirable, it would be quite easy, with an appropriate form of furnace, to refine by distillation considerable quantities of material, as was done by Stas in his classic researches.

The method of distillation in the oxyhydrogen blast

* A Paper read before the Royal Society, April 13, 1905.

employed by Stas suffers from an obvious disadvantage in that he says, after describing the process—"Je dois avouer toutefois que dans les opérations que je viens de décrire la moitié au moins de l'argent employé a été perdue." In addition to avoiding this great loss of material, the liability of the metal to occlude gases would in the new furnace probably be much diminished.

For work on radiation, and as a "black body," some rough preliminary experiments have shown the great advantages of this type of furnace over the carbon tube type, which lasts only a very short time, takes a very large current, and gives off large quantities of poisonous carbonic oxide gas.

For the realisation of the Violle Standard of light, in which the unit is the amount of light given off by 1 sq. cm. of pure platinum at its freezing-point, it is likely a furnace of this type might be very convenient, since it might easily be designed to render possible the desired result with a much smaller quantity of platinum than has hitherto been thought necessary, and at the same time greatly increase the time of solidification, the only period in each experiment during which measurements can be made.

XIV. Conclusion.

In conclusion, I have to thank Mr. Swinburne for several suggestions made at the beginning of the work; Sir William Crookes for kindly replying to queries, and for sending valuable references to the chemical literature of the rare earths forming the tubes; my friends, Mr. R. S. Hutton, lecturer in electro-chemistry at the Manchester University, for references to the American literature; Mr. Sheppard, of the British Nernst Light, Limited, for advice on practical points; and especially Mr. Maurice Solomon, for placing at my disposal valuable knowledge gained in his experience of Nernst filament making. Thanks are also due to Mr. G. Matthey, F.R.S., who provided the very pure metals and alloys used as thermo-junctions; and to the director of the laboratory for provision of special facilities for this research, including the addition to the thermometric department of a specially-designed switch-board and safe regulating resistances for the 250 and 500-volt circuit of the local electric supply.

A list of the more important references to work on electrolytic conductivity and furnaces, and to earlier determinations of the melting-point of platinum is given below.

XV. Bibliography.

List of References to Work on Solid Electrolytes.

Jablochkoff in 1877 showed that half-baked kaolin conducts when hot.

Nernst. British Patent, No. 19424. 1897. A minute hollow cylinder of burnt magnesia will run as a lamp.

Nernst. British Patent, No. 6135. 1898. Deals with differences in behaviour of pure materials and mixtures as lamp filaments. Pure magnesia only works with great difficulty. Best materials for permanence at very high temperatures are zirconia and oxides of the zirconia group.

Nernst and Wild. *Zeitschrift für Electrochemie*, vol. vii., p. 273, December, 1900. "Efficiencies of Various Mixtures as Filaments."

Potter. American Patents.

Nernst. *Göttinger Nachrichten*, 1903, vol. ii., alludes to an attempt to use tubes of solid electrolytic conductors as a furnace for vapour density determinations. He discards these in favour of the iridium tube furnace described.

Nernst. *Zeitschrift f. Electrochemie*, vol. ix., p. 622. Fuller description of same work.

Reynolds. "Gottingen Dissertation," 1903. "Resistance of Solid Electrolytes at High Temperatures."

Literature of Melting-Point of Platinum.

Violle (*Comptes Rendus*, vol. lxxxv., p. 543; and 1881, vol. xcii., p. 866) gives 1775° and 1779° C. as determinations made by his calorimetric method.

Holborn and Wien (*Wied. Annalen*, 1892, vol. xlvii., p. 107; and vol. lvi., p. 360), by thermoelectric method, obtain 1780°.

Nernst (*Physikalische Zeitschrift*, 1903, vol. iv., p. 733; and *Wied. Ann. Beiblätter*, vol. xxv., p. 686) obtains, by an optical method, 1782° as melting-point of platinum in iridium tube furnace.

Older determinations by Becquerel, Van der Weyde, &c., vary between 1400° and 2200° C.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MAY 31ST, 1905.

By SIR WILLIAM CROOKES, F.R.S.,

and
SIR JAMES DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, June 10th, 1905.

SIR,—We submit herewith, at the request of the Metropolitan Water Board, the results of our analyses in detail of samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the Metropolitan Water Board taking their supplies from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from May 1st to May 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 245 samples examined by us during the month, all were clear, bright, and well filtered.

Rain fell at Oxford on eight days only during the month of May. The total amount of rain measured was 0.79 inch; the average for the month is 1.75 inches; thus we have a deficit of 0.96 inch, which, added to the previous one of 0.89 inch, gives a total deficit for this year of 1.85 inches, or 21.2 per cent, on the thirty-five years' average.

Our bacteriological examinations of 415 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 846 others from special wells, standpipes, &c., making a total of 1261 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	147
New River, filtered (mean of 80 samples) ..	16
Thames, unfiltered (mean of 27 samples) ..	1056
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 204 samples) ..	24
Ditto ditto highest	248
Ditto ditto lowest	0
River Lea, unfiltered (mean of 25 samples) ..	205
River Lea, from the East London District clear-water wells (mean of 26 samples) ..	23
Kent District, from the wells at Deptford (mean of 27 samples) ..	2

Of the 337 daily samples taken from the general wells of the Metropolitan Water Board, fifteen samples, or

4.4 per cent, were sterile. Sixteen samples, or 4.7 per cent, contained more than 100 microbes per c.c., and of these five samples contained more than 150 microbes per c.c. The sixteen excess samples contained an average of 1.8 microbes. In April thirteen excess sample contained an average of 1.2 microbes per c.c.

The slight increase of organic matter in the London water observed last month has not been maintained, and the chemical quality is better than it has been for three months past. The microbic condition, although not quite up to the high standard observed in April, is still satisfactory.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

THE STUDY OF ELECTROLYTIC DEPOSITS OF NICKEL.

By M. GRÉSY.

In an examination of the industry of nickel-plating we are first of all struck with surprise at the uncertainty and complexity of the formulæ first proposed, considering the apparent similarity which exists between this operation and that of copper-plating in baths of sulphate of copper; but a closer study of the question soon reveals a primary difference.

In fact, while the presence, in the latter bath, of a fairly large proportion of free sulphuric acid (5 to 10 per cent, for instance) is without practical influence on the quantity of metal deposited per ampère-hour, the least trace of this acid in a free state in the nickel bath destroys the existing theoretical proportion, according to Faraday's law, between these two factors. With a definite and invariable strength of current, all goes on as if the electro-chemical equivalent decreased in proportion as the free acidity increases, while trending rapidly towards zero.

This observation having been made, the idea presented itself of using neutral or ammoniacal solutions of pure sulphate of nickel with soluble nickel anodes; but a second difference then appeared, for, while under these conditions the electrolysis of sulphate of copper is normal and quiet, that of sulphate of nickel is accompanied, on the other hand, with an abundant disengagement of gas from the anode (indicating an incomplete attack of this latter), soon followed by an increasing production of hydrogen at the cathode, and the deposited nickel becomes detached, curling up like wood-shavings, while the electrolyte becomes more and more acid.

This drawback can be corrected in practice, it is true, by neutralising the acid as it is set free, either by means of hydrate or carbonate of nickel freshly precipitated, or again by the addition of ammonia, a method which is more convenient than the former, but having the great inconvenience of impoverishing the bath,* and it may be easily seen that this addition is incompatible with a good commercial process. However, we were lucky in being able to proceed in this manner up to the time when, no doubt by accident, an operator whose name has not come down to us, tired of correcting a recalcitrant bath by the ordinary methods, introduced sea-salt. Immediately the evolution of gas at the electrodes and the acidity began to decrease, and finally disappeared; the current passed more easily on account of the reduction of the counter electromotive force of polarisation, due to the gaseous emanations, the

quantity of metal deposited began to conform with Faraday's law, and the deposit penetrated more deeply than before into the cracks and crevices of the objects under treatment; the workmen interpreted these results in a simple manner by saying that the bath had become more conducting. This, however, does not suffice as an explanation of the whole of the phenomena observed. I therefore undertook a careful examination of the question and arrived at the following results:—

Since the introduction of chloride of sodium or of any alkaline chloride, even chloride of nickel itself, the insufficient attack of the anode gave place to a supersolution of this latter, which loses more weight than the cathode gains, although this cathode receives a deposit conforming with Faraday's law, and we observe a basic reaction of the electrolyte by means of litmus-paper; then there is produced a cloudiness which becomes more pronounced, until eventually a greenish yellow mud is deposited which has all the characteristics of an oxide of nickel no doubt hydrated.

Finally, however it may be, in spite of this change in the electrolyte, the deposit is produced for a long time in a satisfactory manner, which constitutes a great improvement in the successful commercial use of the nickel plating bath.

There arrives a time, however, when the colour of the deposit becomes darker; then there is a want of adherence, and the metal becomes detached in small scales; it suffices at this point to re-acidulate the bath slightly for the process to return to its normal state.*

This closes my remarks, which, while giving to practical men a simple explanation of an interesting stage of a chemical process taking place in the nickel-plating bath, will also, I hope, tend to diminish their too general habit of using empirical corrections.—*Moniteur Scientifique*, June, 1905, p. 428.

THE ESTIMATION OF LEAD AND ANTIMONY IN THE FORM OF SULPHIDE.

By J. A. MULLER.

ESTIMATIONS of lead and antimony in the form of sulphide are operations of common occurrence in laboratories. These estimations, however, are not as a general rule very exact. As far as sulphide of lead is concerned, we know that this body when heated in the air, slowly increases in weight, even at so low a temperature as 100°; on the other hand, the estimation by H. Rose's method in a current of pure dry hydrogen is rather delicate for ordinary use, for by heating a little too strongly there is a loss of weight (1) by volatilisation of a little of the sulphide; (2) through a loss of sulphur. Sulphide of antimony dried at 100° may still retain up to 2 per cent of water, and it may also contain free sulphur. We therefore generally determine the amount of Sb₂S₃ contained in the precipitate by heating an aliquot part in a current of carbonic anhydride, until the transformation into black sulphide is complete; if it contains free sulphur, it is necessary to heat a little more strongly to volatilise it, but it is preferable to transform the whole of the sulphide into tetroxide, and to estimate the antimony in this form.

Instead of following the above methods for effecting the estimation of lead and antimony, I propose to estimate these metals in the form of sulphides by proceeding in the following manner:—The precipitates obtained by treating the corresponding solutions with sulphuretted hydrogen in hot acid solution are thrown on tared filters, and then

* We know, in fact, that the ammoniacal sulphate of nickel, formed under these conditions at the expense of the simple sulphate of nickel present in the bath, is almost insoluble in a concentrated solution of sulphate of ammonia, which occurs eventually when we make use of this method of correction, and the whole of the nickel in the bath is thus almost entirely eliminated, leaving only an inactive solution of sulphate of ammonia.

* We must avoid the use of organic acids which only cause a temporary acidity, both they and their salts being decomposed by the passage of the current. Sulphuric acid answers very well. Many nickel-platers use boric acid, which has the property of enhancing the whiteness of the deposit, but not more than 10 grms. per litre must be added, or the deposit will commence to come off. Further, it does not dispense with the necessity for using sulphuric acid.

washed (1) with sulphuretted hydrogen water, (2) with alcohol at 95 per cent, (3) with a mixture of equal volumes of alcohol at 95 per cent, ether, and sulphide of carbon, (4), with absolute ether; the double filters are then dried *in vacuo* over sulphuric acid, and weighed.

With the object of verifying this method for the estimation of lead and antimony, I have made the two following series of experiments:—

Control Estimation of Lead in the Form of Sulphide.—I prepared a solution of nitrate of lead, which gave me, for a volume of 40.03 c.c. at 19.5°, 2.6265 grms. of PbSO₄ on precipitating the solution with a slight excess of dilute sulphuric acid, and then adding gradually while stirring sufficient alcohol to obtain a solution of 70 per cent alcohol by volume. I then took samples of 40.03 c.c., 30.11 c.c., 20.05 c.c., 10.06 c.c., and 5.00 c.c. of this solution of nitrate, and after having diluted these separate quantities up to 400, 300, 300, 200, and 150 c.c. respectively with water containing about 1 per cent of nitric acid of density = 1.3, they were saturated with sulphuretted hydrogen after heating to about 35°. The precipitates formed were thrown on to tared filters, and then washed and dried as has been described above.

To avoid all possible errors due to the filters, these were first washed with the mixture of alcohol, ether, and sulphide of carbon, then with pure ether; after desiccation over sulphuric acid and then in the oven, the weights of each pair were equalised as closely as possible in the balance, one being placed in each pan (Curie's method).

After having left the two filters for about an hour in the closed balance case so as to allow the paper to reach hygrometric equilibrium with the atmosphere in the latter, the small difference in weight between them was determined as accurately as possible without opening the case.

After having weighed the dried sulphides they were transformed by nitric oxidation into sulphates of which the weights were taken after each transformation.

These weights were respectively as follows:—2.6266 grms., 1.9733 grms., 1.3187 grms., 0.6602 grm., and 0.3258 grm. On treating these sulphates with sulphuric acid and calcining at a dull red heat, the same weights were obtained to within 0.2 m.grm.

To sum up, the following were the results obtained in tabular form:—

a.	b.	c.
Weight of PbS washed and dried <i>in vacuo</i> for forty-eight hours.	Weight of PbS calculated from the estimation of the lead in the 40.03 c.c. and the volumes of the different treatments.	Weight of PbS calculated from that of the PbSO ₄ resulting from the nitric oxidation of the sulphides.
Grms.	Grms.	Grms.
2.0738	2.0717	2.0717
1.5605	1.5583	1.5565
1.0382	1.0375	1.0402
0.5192	0.5208	0.5208
0.2573	0.2588	0.2570

By adopting for the weight of PbS we ought to have found, the mean of the figures in columns *b* and *c*, we find that the direct weighing of the sulphide dried *in vacuo* has given respectively 100.1, 100.2, 99.9, 99.7, and 99.8 per cent.

Control Estimation of Antimony in the Form of Sulphide.—We first prepared pure sulphide of antimony by precipitating a hydrochloro-tartaric solution of pure oxychloride of antimony with sulphuretted hydrogen. After having washed the precipitate as described above, it was dried *in vacuo* over sulphuric acid, and then divided into four unequal parts, which were placed in porcelain boats for the purpose of heating them in a current of pure dry carbonic acid. The black sulphides in the boats were dissolved in hot fuming hydrochloric acid, taking care not to lose any antimony during this operation. The hydrochloric solutions were then treated with tartaric acid and about 450 c.c. of water, and then saturated with sulphuretted hydrogen

after having been heated gently. The precipitates were washed in the usual manner, using the filter-pump for the most voluminous. Neither the filtered hydrochloric solutions nor the sulphocarbonic solutions contain any antimony. In the same way as with lead, each filter containing a precipitate was withdrawn from its funnel after washing, and placed in a flat crucible under a bell-jar, in which the acid (about 2 kilos.) was renewed after one day's desiccation; they were left in dry *vacuo* for two days.

The following results were obtained:—

Weight of Sb ₂ S ₃ dissolved in HCl.	Weight of Sb ₂ S ₃ washed and dried <i>in vacuo</i>
Grm.	Grm.
0.8975	0.9025
0.5841	0.5873
0.2844	0.2849
0.0942	0.0940

Thus we found, respectively, 100.6, 100.5, 100.2, and 99.8 per cent.—*Bull. Soc. Chim.*, Series, 3, vol. xxxi., No. 24.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, June 1st, 1905.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

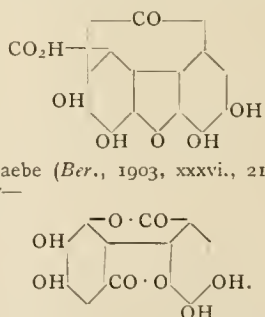
(Concluded from p. 278).

113. "Estimation of Hydrogen Peroxide in the presence of Potassium Persulphate." By JOHN ALBERT NEWTON FRIEND.

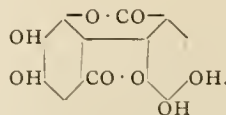
The author has already shown that hydrogen peroxide cannot be correctly estimated in ordinary circumstances by titration with potassium permanganate in the presence of potassium persulphate (*Trans.*, 1904, lxxxv., 597). The amount of permanganate required always falls short of the theoretical. The author now shows that if a slight excess of permanganate is rapidly added from a burette to the mixture of peroxide and persulphate, and the excess of permanganate estimated iodometrically with thiosulphate, very accurate results may be obtained in the presence of any weight of potassium persulphate not exceeding 0.08 grm.

114. "Some Oxidation Products of the Hydroxybenzoic Acids and the Constitution of Ellagic Acid." By ARTHUR GEORGE PERKIN and MAXIMILIAN NIERENSTEIN.

When gallic acid dissolved in sulphuric acid is treated with potassium persulphate with or without boric acid, ellagic acid, C₁₄H₆O₈, is formed (yield, 67 per cent approximately), a substance to which Goldschmidt and Barth (*Ber.*, 1879, xii., 1237) and Goldschmidt and Jahoda (*Monatsh.*, 1892, xiii., 51) gave the constitution—



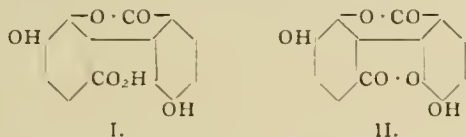
but which Graebe (*Ber.*, 1903, xxxvi., 212) considers is more probably—



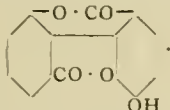
Tetra-acetyllellagic acid, C₁₄H₂O₈(C₂H₃O₂)₄, sinters at about 305° and melts at 313–316°. Protocatechuic acid,

in a similar manner, gives a compound, $C_{14}H_6O_6$, probably identical with Schiff's catellagic acid (*Ber.*, 1882, xv., 2590), which he prepared by means of arsenic acid and for which he suggested either of the formulæ $C_{14}H_{10}O_7$ and $C_{14}H_8O_7$. This compound was obtained by the author as minute colourless needles, melting above 360° , subliming at higher temperatures, and gave the diacetyl derivative, $C_{14}H_4O_6(C_2H_3O)_2$ (prismatic needles, m. p. $322-324^\circ$). On distillation with zinc dust, it resembles ellagic acid in giving fluorene.

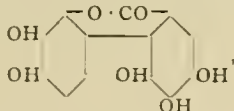
From the product of the oxidation of *p*-hydroxybenzoic acid in the same manner, catellagic acid, $C_{14}H_8O_6$ (colourless silky needles, m. p. above 360°), and a trace of protocatechuic acid have been isolated. The substance $C_{14}H_8O_6$ gives a diacetyl compound, $C_{14}H_6O_6(C_2H_3O)_2$ (long colourless needles, m. p. $267-268^\circ$) and yields fluorene on distillation with zinc dust, and by fusion with alkali two compounds, probably acids, which are still under examination. To this compound, $C_{14}H_8O_6$, which appears to result from the interaction of *p*-hydroxybenzoic acid and protocatechuic acid, the constitution I. is assigned, from which that of catellagic acid follows (II.). By analogy, ellagic acid can be similarly formulated, pointing strongly to the correctness of Graebe's suggestion (*loc. cit.*).



When oxidised by this method, *m*-hydroxybenzoic acid gives a complex mixture of yellow crystalline substances and a yellow dyestuff not yet obtained crystalline, but there is also present a compound, $C_{14}H_6O_5$ (colourless needles, m. p. $273-276^\circ$), subliming at higher temperatures, which is termed metellagic acid. The monoacetyl derivative, $C_{14}H_5O_5 \cdot C_2H_3O$ (colourless leaflets, m. p. $269-271^\circ$), has been prepared, and by distillation with zinc dust a hydrocarbon resembling fluorene is produced. The following constitution is assigned to this substance:—



By the action of caustic potash on ellagic acid, Barth and Goldschmidt (*loc. cit.*) obtained hexahydroxydiphenylene ketone (?), $C_{13}H_8O_7$, and hexahydroxydiphenyl. It is now shown that the former compound gives the *penta*-acetyl derivative, $C_{13}H_3O_7(C_2H_3O)_5$ (small colourless prisms, m. p. $217-219^\circ$), and the *pentabenzoyl* derivative, $C_{13}H_3O_7(C_7H_5O)_5$ colourless plates, m. p. $257-259^\circ$). Its constitution must accordingly be—



as surmised by Graebe (*loc. cit.*), and this further confirms the above results.

On oxidation by this method, salicylic acid gives a product insoluble in water, and this result is being investigated together with the behaviour of other acids in this respect.

115. "The Reduction of Isophthalic Acid." (Part II.). By WILLIAM LAWTON GOODWIN and WILLIAM HENRY PERKIN, jun.

The authors describe a convenient method for the preparation and separation of the *cis*- and *trans*-modifications of hexahydroisophthalic acid, and show that the acid melting at $120-122^\circ$ (Perkin, *Trans.*, 1891, lix., 814;

Baeyer and Villiger, *Annalen*, 1893, cclxxvi., 255), which has so far been assumed to be pure *trans*-hexahydroisophthalic acid, is, in reality, a mixture of about equal quantities of the *cis*- and *trans*-modifications. This mixture cannot be resolved by crystallisation, but treatment with calcium chloride and excess of ammonia on the water-bath causes the whole of the *cis*-acid to separate in the form of the sparingly soluble calcium salt, and the pure *trans*-acid is then obtained from the mother-liquors.

cis-Hexahydroisophthalic acid melts at $162-163^\circ$ and the *trans*-modification at 148° . These acids are partially converted into one another by heating with hydrochloric acid at 170° , and the *trans*-acid is completely converted into the anhydride of the *cis*-acid when it is heated with acetyl chloride at 150° . The action of bromine on these acids has been investigated, and the behaviour of mono- and di-bromo-*trans*-hexahydroisophthalic acids, on treatment with alkalis, is discussed in detail.

116. "Complex Ammonium Antimonious Halides." By ROBERT MARTIN CAVEN.

Numerous double or complex alkali antimonious halides have previously been described (H. L. Wells and F. J. Metzger, *CHEMICAL NEWS*, 1901, lxxxiv., 194). The existing types exhibit the following molecular ratios of alkali to antimonious halide, with or without water of crystallisation:—4:1, 3:1, 7:3, 2:1, 3:2, 1:1, 3:4, 4:7, 1:2, 1:3.

The following new salts have now been prepared:—

$7NH_4Br \cdot 3SbBr_3$, pale yellow, hexagonal plates (found, $NH_4 = 7.18$; $Sb = 20.39$; $Br = 72.39$; calculated, $NH_4 = 7.13$; $Sb = 20.42$; $Br = 72.45$ per cent).

$3NH_4Br \cdot 2SbBr_3$, bright yellow prisms (found, $NH_4 = 5.44$; $Sb = 23.52$; $Br = 70.94$; calculated, $NH_4 = 5.32$; $Sb = 23.72$; $Br = 70.97$ per cent).

$3NH_4I \cdot 2SbI_3$, deep red, tetragonal plates (found, $NH_4 = 3.75$; $Sb = 16.70$; $I = 79.24$; calculated, $NH_4 = 3.76$; $Sb = 16.74$; $I = 79.49$ per cent).

The double iodide had previously been obtained crystallising with $3H_2O$; the anhydrous compound is sensitive to light, the surface of a small quantity kept in a tube placed in a desiccator over sulphuric acid becoming light brown after some weeks.

The method of preparation of these salts consists in adding excess of glacial acetic acid (99–100 per cent) to a concentrated aqueous solution of the two halides and the halogen acid, the complex salt quickly separating in a well crystallised condition. The same complex iodide always resulted, although the two constituent salts were mixed in varied proportions.

In the case of the bromides, the bright yellow salt was only obtained free from admixture with the pale salt when an amount of antimonious bromide in excess of that indicated by the formula was employed.

These salts, unlike ammonium platinichloride, are easily soluble in absolute alcohol, and, in the case at least of the bromides, the colours of their solutions in this solvent, as well as in the corresponding halogen acid, show that they do not break up considerably into their constituents when dissolved. Ammonium halide slowly separates from cold alcoholic solution, and evaporation gives rise to a mixture. An alcoholic solution of the pale bromide becomes darker when heated, but returns to its original colour on cooling; the bright yellow salt also forms a pale solution which darkens on heating. Thus it appears that two complex salts can exist in solution, a transition from one to the other taking place with change of temperature.

117. "The Replacement of Hydroxyl by Bromine." By WILLIAM HENRY PERKIN, jun., and JOHN LIONEL SIMONSEN.

The preparation of compounds containing several atoms of bromine, by the action of hydrobromic acid on the corresponding alcohols, gives frequently very unsatisfactory results, not only because the reaction is usually incomplete, but also because considerable decomposition and formation of carbonaceous matter nearly always takes

place. The authors find that much more satisfactory results are obtained when the acetate of the alcohol is heated at about 150° , with a solution of hydrogen bromide in acetic acid (saturated at 0°).

The following cases have been studied:—

Triacetin yields *s*-tribromopropane, $\text{CH}_2\text{Br}-\text{CHBr}-\text{CH}_2\text{Br}$. Erythritol tetracetate yields *s*-tetrabromobutane, $\text{CH}_2\text{Br}-\text{CHBr}-\text{CHBr}-\text{CH}_2\text{Br}$.

Penterythritol tetracetate, $\text{C}(\text{CH}_2\text{O}-\text{C}_2\text{H}_3\text{O})_4$, yields *s*-tetrabromotetramethylmethane, $\text{C}(\text{CH}_2\text{Br})_4$, and tribromotrimethylcarbinyl acetate, $(\text{CH}_2\text{Br})_3\text{C}-\text{CH}_2\text{O}-\text{C}_2\text{H}_3\text{O}$.

Mannitol hexacetate is converted into pentabromohexyl acetate, $\text{C}_6\text{H}_5\text{Br}_5(\text{O}-\text{C}_2\text{H}_3\text{O})$, and in this case it was not found possible to remove the remaining acetyl group even when the substance was heated at 170° for several hours with the acetic acid solution of hydrogen bromide.

118. "The Ethereal Salts and Amide of Dimethoxypropionic Acid Derived from *d*-Glyceric Acid." By PERCY FARADAY FRANKLAND and NORMAN LESLIE GEBHARD.

The authors describe the preparation and properties of methyl, ethyl, propyl, butyl, heptyl, and octyl dimethoxypropionates, which they have obtained by the direct methylation by Purdie's method (*Trans.*, 1899, lxxv., 153 and 483) (methyl iodide and silver oxide) of the corresponding ethereal salts of *d*-glyceric acid.

The *d*-glyceric esters are all laevorotatory, as are also the corresponding dimethoxypropionates, the latter having, however, a much higher molecular rotation, whilst the molecular rotations of the di-acetylglycerates, di-propionylglycerates, di-monochloroacetylglycerates, di-dichloroacetylglycerates, di-trichloroacetylglycerates, and di-phenylacetylglycerates are intermediate between the two.

As in the case of the glycerates, the molecular rotation in the normal series attains a maximum in either the amyl, hexyl, or heptyl term (the normal amyl and hexyl terms being still unknown, the highest molecular rotation actually observed is that of the heptyl ester).

Tables are given comparing the molecular rotations of lactic and glyceric derivatives, on the one hand, and of malic and tartaric derivatives on the other.

The amide and methylamide of dimethoxypropionic acid have also been prepared. The amide has a higher molecular rotation (laevo) than glyceramide, whilst that of the methylamide is higher still.

The esters of dimethoxypropionic acid have their rotation diminished by rise of temperature, whilst the latter increases the rotation of the glycerates and diacetylglycerates.

119. "The Influence of Phosphates on the Fermentation of Glucose by Yeast Juice." (Preliminary communication). By ARTHUR HARDEN and WILLIAM JOHN YOUNG.

It has previously been shown by the authors (*Journ. Physiol.*, 1904, xxxii.; *Proceedings*, Nov. 12th) that the amount of glucose fermented by a given volume of yeast juice is greatly increased by the addition of boiled and filtered yeast juice.

When the rates of evolution of carbon dioxide are compared from (1) a mixture of yeast juice and glucose, and (2) a similar mixture to which boiled and filtered yeast juice has been added, it is found that two phenomena are concerned in the production of this increased fermentation in the presence of boiled yeast juice:—

(a) The addition of the boiled juice produces an initial rapid evolution of carbon dioxide, which soon diminishes until a rate is attained which remains constant for many hours.

(b) This steady rate is usually, but not invariably, approximately equal to that given by an equal volume of the same yeast juice and sugar to which no addition has been made, but diminishes more slowly than this, so that the fermentation continues for a longer period.

The greater proportion of the total increase is usually due to this second phenomenon.

A similar initial rapid evolution of carbon dioxide occurs when a solution of sodium or potassium orthophosphate is

added instead of the boiled juice, but in this case no marked prolongation of the fermentation is observed.

The extra quantity of carbon dioxide evolved in this initial period may be calculated by subtracting the amount corresponding with the constant rate from the total amount observed. It is then found that this quantity corresponds with the evolution of one molecular proportion of carbon dioxide for every atom of phosphorus added in the form of sodium or potassium orthophosphate, or present in the boiled juice in a form precipitable by magnesia mixture. The greatest amount of carbon dioxide hitherto obtained in this way from 25 c.c. of yeast juice is 0.46 grm., corresponding with the addition of about 1.5 grms. of anhydrous disodium hydrogen phosphate.

Ordinary yeast juice itself contains a certain amount of dissolved phosphate, and hence, when sugar is added to it, the same phenomenon of an initial rapid evolution of carbon dioxide is observed, but it is usually small in amount.

This evolution of carbon dioxide is accompanied in all cases by the production of an equimolecular proportion of alcohol, and represents the alcoholic fermentation of a corresponding amount of glucose.

When the liquid in which fermentation has been carried on in presence of phosphate is boiled and filtered, the added phosphorus is found in the filtrate, but it is no longer in a form precipitable by magnesia mixture or silver nitrate. The exact mode of combination of this phosphorus in the filtrate and in the unboiled liquid has not yet been definitely ascertained.

Many other questions of interest arise in connection with this phenomenon, and the whole subject is still under investigation.

120. "A Contribution to the Study of Alkylated Glucosides." By JAMES COLQUHOUN IRVINE and ADAM CAMERON.

By alkylating β -methylglucoside by means of silver oxide and methyl iodide, tetramethyl β -methylglucoside was produced, which was shown to be identical with the crystalline pentamethylated glucose previously obtained by the methylation of tetramethyl glucose. This confirms the idea that the alkylation of this sugar results in the formation of two isomeric alkylated glucosides which correspond respectively to α - and β -methylglucosides. The specific rotations of the completely methylated β -methylglucoside in water, alcohol, acetone, and benzene proved to be -17.34° , -17.43° , -18.07° , and -16.56° respectively.

The interconversion of α - and β -tetramethylmethyl glucosides was carried out by heating either form with solutions of hydrogen chloride (0.25 per cent) in methyl alcohol, acetone, ether, or benzene, the change being more rapid in alcohol than in the other solvents. In the absence of hydrogen chloride, no transformation took place.

Tetramethyl β -methylgalactoside was also prepared by alkylating β -methylgalactoside, and proved to be identical with the crystalline pentamethylated galactose already described (*Trans.*, 1904, lxxxv., 1071), and thus the nature of the latter compound is established. In the course of this work a fully methylated galactoside was obtained which differed from the well-defined α - and β -isomerides in displaying a very low dextrorotation, and in showing comparatively small changes in rotatory power when hydrolysed.

Atomic Weight of Nitrogen deduced from the Proportional Densities of Nitrogen and Oxygen.—Philippe A. Guye.—The author applies the law that the densities of gases determined under corresponding conditions of temperature and pressure, reduced to 0° and one atmosphere pressure by the formula for perfect gases, are rigorously proportional to the molecular weights of these gases, to the determination of the atomic weight of nitrogen from calculations of the relative densities of oxygen and nitrogen, and he finds as a mean value 14.009, taking O as 16.—*Comptes Rendus*, cxl., No. 21.

NOTICES OF BOOKS.

The Preservation of Antiquities. By Dr. FRIEDRICH RATHGEN. Translated by GEORGE A. AUDEN, M.A., M.D. (Cantab.), and HAROLD A. AUDEN, M.Sc. (Vict.), D.Sc. (Tubingen). Cambridge: The University Press. 1905.

In this book, which merits the attention of curators of museums and antiquarians, the Director of the Laboratory of the Royal Museums, Berlin, in a very scholarly manner, treats of the best and most reliable means of preserving antiquities of various kinds. The changes undergone by objects made both of inorganic and organic substances are discussed from a scientific point of view, and full directions are given for preserving them by methods differing according to circumstances. An excellent tabulated summary gives a clear view of the various methods of preservation and their applicability, the procedure advocated being in all cases simple and yet capable, as the illustrations show, of giving excellent results. Various practical suggestions are added for the care of antiquities after preservative treatment, and the translators add appendices on Reinach's method of taking squeezes of inscriptions, &c., and also on the use of the preparation "Zapon" for the protection of metals from oxidation and from the action of sulphuretted hydrogen.

Naturkonstanten. ("Constants of Nature"). Edited by Professor Dr. H. ERDMANN and Privatdozent Dr. P. KOTHNER. Berlin: Julius Springer. 1905.

A LARGE amount of information of a very useful nature is contained in this collection of tables, and the book possesses some peculiar merits which will no doubt be appreciated by physicists and chemists. Chief among these merits must be mentioned the excellence of the arrangements which have been made to enable the reader to lose no time in discovering the information he requires. The thumb index in the margin greatly facilitates rapid reference to the various tables, and in addition a complete alphabetical index is given at the end of the book. As regards the data contained in the collection the authors have preferred as far as possible to exercise their critical faculties, and to include what they consider the most reliable numbers, if not always those obtained as the results of the most recent experiments. Some of the numbers given, however, require revision, as, for instance, some of the gas constants, and the addition of more tables of technical analysis, such as Kjeldahl tables, would be an advantage for general use. The inclusion of data for spectral analysis is a specially useful feature, not always to be found in such works.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxi., No. 21, May 22, 1905.

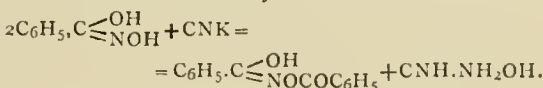
Compressibility of different Gases at Pressures of less than One Atmosphere, and the Determination of their Molecular Weights.—Adrien Jaquero and Otto Scheuer.—The determination of the compressibility of gases at pressures less than one atmosphere is of great importance as a means of obtaining their exact molecular weight by the method of limit densities (L_0). The limit density can be deduced from the weight of a normal litre of the gas (L). These calculated molecular weights practically coincide with results obtained by the best analytical methods.

Fusibility of Mixtures formed by Antimony Sulphide with Cuprous Sulphide and Mercuric Sulphide.—H. Pélabon.—Cuprous sulphide (Cu_2S) and mercuric sulphide (HgS) will dissolve in antimony sulphide if this is melted and kept at a sufficiently high temperature. The author makes a series of experiments on the fusibility of the substances thus obtained.

Equilibrium between Acetone and Hydroxylamine Chlorohydrate.—Philippe Landrieu.—The author determines the limits of the equilibrium produced during the reaction of acetone on hydroxylamine chlorohydrate and the variations of this limit with dilution:— $\text{Acetone (diss.)} + \text{NH}_4\text{OCl (diss.)} = \text{Oxime HCl (diss.)} + \text{H}_2\text{O}$.

Action of Ammonium Metals on the Polyatomic Alcohols.—E. Chablay.—When ammonium metals act on the polyatomic alcohols, it is of importance to measure the quantity of hydrogen evolved, since this shows the degree of substitution effected. The author investigates this reaction in the particular cases of mannite and erythrite. He also prepares the sodium derivatives of menthol and borneol. These two alcohols are very soluble in liquid ammonia. By reason of their secondary alcohol function they act more energetically than mannite or erythrite. In the case of the alcohols of the fatty series derived from the non-saturated hydrocarbons different results were obtained, which the author intends to further investigate.

Benz-hydroxamic and Dibenz-hydroxamic Acids. R. Marquis.—In presence of certain bodies capable of combining with hydroxylamine, 2 molecules of benz-hydroxamic acid lose 1 molecule of hydroxylamine and form 1 molecule of dibenz-hydroxamic acid:—



This fact is particularly remarkable, since benz-hydroxamic acid is very stable towards acids, even concentrated sulphuric acid at ordinary temperatures.

New Method of Preparation of the Mesoxalic Ethers; their Condensation with Cyanacetic Ethers. Ch. Schmitt.—The author prepares the mesoxalic ethers with a yield of 65 per cent by passing a current of nitrous vapours through the corresponding malonic ethers in presence of acetic anhydride and ether, using the method employed by MM. Bouveault and Wahl to obtain ethyl diketo-butyrate from acetylacetic ether.

Basicity of Pyranic Oxygen. Double Halogen Salts of certain Metals and Dinaphthopyryl.—R. Fosse and L. Lesage.—In certain compounds the organic non-nitrated radicle dinaphthopyryl, $-\text{CH} < \begin{smallmatrix} \text{C}_{10}\text{H}_6 \\ \text{C}_{10}\text{H}_6 \end{smallmatrix} < \text{O}$, plays the same part as an atom of an alkaline metal, such as potassium. This analogy between potassium and pyryl is especially interesting if the formulæ of potassium chloroplatinate and dinaphthopyryl chloroplatinate are compared—the latter being the first known type of a new class of double salts of oxygen:— $\text{PtCl}_4 + 2\text{Cl} - \text{K}, \text{PtCl}_4 + 2\text{Cl} - \text{O} < \begin{smallmatrix} \text{C}_{10}\text{H}_6 \\ \text{C}_{10}\text{H}_6 \end{smallmatrix} > \text{CH}$. The same view can also be taken of the formulæ of certain new double salts described in this paper—the metallic dinaphthopyryls.



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THE CHEMICAL NEWS.

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EQUILIBRIA IN THE SYSTEMS $\text{TINO}_3\text{--KNO}_3$, $\text{TINO}_3\text{--AgNO}_3$,† AND $\text{TINO}_3\text{--NaNO}_3$.

By C. VAN EYK.

$\text{TINO}_3\text{--KNO}_3$.

THE investigation of this system has already been described (*Zeit. f. Physik. Chem.*, 1899, xxx., 430). In further experiments on the formation of mixed crystals of TINO_3 and other nitrates, besides the transition-point of the TINO_3 at 142.5° (dilatometrically) a second transition-point at 72.8° (dilatometrically) was observed.

This last transition must thus occur also in the mixed crystals of KNO_3 and TINO_3 , and was not observed by me previously.

Transition Temperatures of TINO_3 .—It has been shown by more recent experiments that TINO_3 solidifies in regular crystalline form. At 142.5° a transition occurs into the rhombohedral, and at 72.8° a second transition into the rhombic modification. This last transition-point may easily be overlooked because the transition process is very slow. As the temperature falls the overstepping of the transition temperature may be very considerable. Thus it is not possible to observe the transition thermometrically. Moreover, it can easily be overlooked when the dilatometric method is employed because the change of volume is very small.

I have established a small increase of volume (± 0.0004 c.c. per 1 grm. TINO_3) accompanying the transition rhombic—rhombohedral. As no new method was employed the details of the determinations are omitted in the following experiments:—

In my former experiments, carried out by the optical method on the transitions of the mixed crystals $\text{KNO}_3\text{--TINO}_3$, I did not observe the transition at 72.8° . These optical experiments were performed with very thin layers of the salt mixture which had solidified on an object glass (*Zeit. f. Physik. Chem.*, 1899, xxx., 446). The lag is then so great that the transition as the temperature falls does not occur for hours, and sometimes for days.

After I had found that at 72.8° a change of volume takes place, I was able to observe this change by the optical method also, if the layer of solidified TINO_3 was made less thin, or if a layer of increasing thickness was taken. Nevertheless, the lag of this transition is so great and the rate of transition so small that the temperature can only be determined accurately if the transition is allowed to take place a few times in each direction. For example, the object glass is heated to 85° , at which temperature the transition takes place. If after cooling the TINO_3 had again become rhombic the object glass was heated to 84° . Thus it was continually heated to lower and lower temperatures till finally a temperature was reached at which even after several hours no transition was observed. It was thus found that the transition temperature lay between 79° and 80° .

Transition of the Mixed Crystals of $\text{TINO}_3\text{--KNO}_3$.—The molten mixture of TINO_3 with 0 to 33 mols. per cent KNO_3 deposits regular mixed crystals of TINO_3 with 0 to 20 mols. per cent KNO_3 .

The molten mixture of KNO_3 and 0 to 67 mols. per cent TINO_3 deposits rhombohedral mixed crystals of KNO_3 with 0 to 50 mols. per cent TINO_3 .

The solid mixtures of 20 to 50 mols. per cent KNO_3 at 182° form a conglomerate of regular mixed crystals with 20 mols. per cent KNO_3 and rhombohedral mixed crystals with 50 mols. per cent KNO_3 .

The limits of separation are extended as the temperature falls; at 133° the mixture limits of the regular and rhombohedral crystals are 20 and 69 mols. per cent KNO_3 .

The transition of the regular mixed crystals of 0 to 20 mols. per cent KNO_3 into rhombohedral mixed crystals takes place at 144.5° to 133° .

The transition of the rhombohedral mixed crystals with 0 to 16 mols. per cent TINO_3 occurs at 129.5° to 108.5° .

Below 133° to 108.5° conglomerates with two kinds of rhombohedral mixed crystals were formed.

The determination of this transition has already been described (*Zeit. f. Physik. Chem.*, 1899, xxx., 446).

The rhombohedral mixed crystals (see Fig. 1) with 0 to 25 mols. per cent KNO_3 will again be converted when the temperature falls into rhombic mixed crystals.

The transition temperatures were determined by the optical method, as was described above in the case of the transition-point of TINO_3 .

TINO_3 , mols. per cent.	Transition temperature.
100	79°
92.6	82.5°
80.6	86°
76.5	86°
69.3	86°
59.4	86°

In mixtures with small amounts of TINO_3 the transition temperature cannot be determined.

The transition of the mixed crystals was also determined by the dilatometric method.

TINO_3 , mols. per cent.	Transition temperature.
100	72.8°
95.6	75°
85.4	77.5°
75.3	78.4°
64.5	78°

As the expansion at the transition is very small the transition temperature could not be determined further in this case also.

The transition of the rhombohedral mixed crystals with 100 to 81 mols. per cent TINO_3 thus occurs between 72.8° and 78° .

Below 108.5° to 78° we have a conglomerate of rhombohedral and rhombic mixed crystals, and below 78° a conglomerate of two kinds of rhombic mixed crystals.

$\text{TINO}_3\text{--AgNO}_3$.

In the literature of the subject I have found no accounts of the formation of mixed crystals of TINO_3 and AgNO_3 . Retgers mentions a double salt without saying how he had obtained this double salt, whether from the aqueous solution or from the fused mixture (*Zeit. f. Physik. Chem.*, 1890, v., 451).

I undertook the investigation of this system in the hope of finding a system in which double salt and mixed crystals exist side by side, and moreover—because the transition-points of TINO_3 and AgNO_3 fall in the region of the solidification curve—I hoped to obtain an example of the melting of a binary mixture by cooling, as it was observed by de Kock (*Dissert.*, Amsterdam, 1903). The result, however, was negative, because on solidifying a double salt was deposited from the fused mixture, but no mixed crystals.

Determination of the Solidification Curve.—The solidification temperatures were determined in the same way as was described before (*Zeit. f. Physik. Chem.*, 1899, xxx., 431). But they sink very rapidly towards both sides, and between these two descending parts of the curve of solidification lies a very small double salt curve.

* *Zeit. f. Physik. Chem.*, 1899, xxx., 430.

† *Verlag Koninkl. Akad. van Wetenschappen, Amsterdam, Feb., 1900.*

AgNO ₃ , mols. per cent.	Commencement of solidification.
100	208.5°
94	196°
90	188.5°
87	183°
86	181°
78.5	161.5°
70.5	140°
68	133°
62	116°
54	91°
53	85°
52	81.6°
50	82.8°
48	81.2°
47	85°
41.5	100.6°
40.5	105°
37.5	112°
30.7	129°
22.5	149°
14	173.5°
0	200°

The graphic representation (Fig. 2) shows this better.

The determination of the points of section (at $\pm 81^\circ$) of the curves of AgNO₃ and of TlNO₃ with the curve of the double salt AgNO₃TlNO₃ is not easily performed accurately because super-cooling always takes place. The beginning of solidification of a mixture of 47 mols. per cent AgNO₃, for example, occurs at a temperature of 85°. At this temperature crystals separate out which are heavier than the melt. The separation of the crystals continues with falling temperature until considerably below 80°, then a large amount of double salt appears all at once, and the temperature rises to 82.8°.

This sudden separation of the double salt does not always occur at the same temperature. This temperature frequently lies below 70°. The same thing was observed in mixtures which contained more than 50 mols. per cent AgNO₃. A mixture with, for example, 53 mols. per cent AgNO₃ deposits the first crystals at 83.5°; these crystals are lighter than the melt. Frequently crystals are deposited below 75° or a lower temperature until a great quantity of crystals again separates out suddenly, and the temperature rises to 82.8°. This is the maximum temperature which has been observed. In different observations with the same mixture this temperature varies from 82 to 82.8°. In the many determinations of the solidification temperature of the mixtures with 40 to 60 mols. per cent TlNO₃, I have only once observed that the temperature did not rise to 82.8°, but only to 74.6°, and the whole salt mixture solidified at this temperature. I observed this in a mixture of 39.5 mols. per cent TlNO₃. The experiment proceeded as follows:—Solidification began at 110.8°, the temperature sank steadily to 73°, while crystals separated out which were lighter than the melt. Then the temperature rose suddenly to 74.6°, and remained constant until the whole had become solid. The thermometers within and outside the bath were read off every minute.

I also observed the same thing with a mixture with a higher solidification temperature; for example, in a mixture with 22.4 mols. per cent AgNO₃, which begins to solidify at 149°. The temperature sank steadily to 72°, rose suddenly to 74°, and remained constant at this point for some time. This phenomenon may probably be explained as follows:—In this case no double salt separates; the temperature 74.6° is probably the eutectic point, the point of section of the two solidification curves of TlNO₃ and AgNO₃. That is to say, if these two curves are produced downwards they intersect in a point which must lie at $\pm 75^\circ$.

The following observations agree with this:—I have frequently observed that in a mixture of, for example, 60 mols. per cent TlNO₃, the temperature sank to 72° (or even lower), while it deposited crystals, then suddenly rose to

74.6°, remained constant at that point for some minutes, and then suddenly rushed up to $\pm 82^\circ$. The temperature then remained constant till all was solidified.

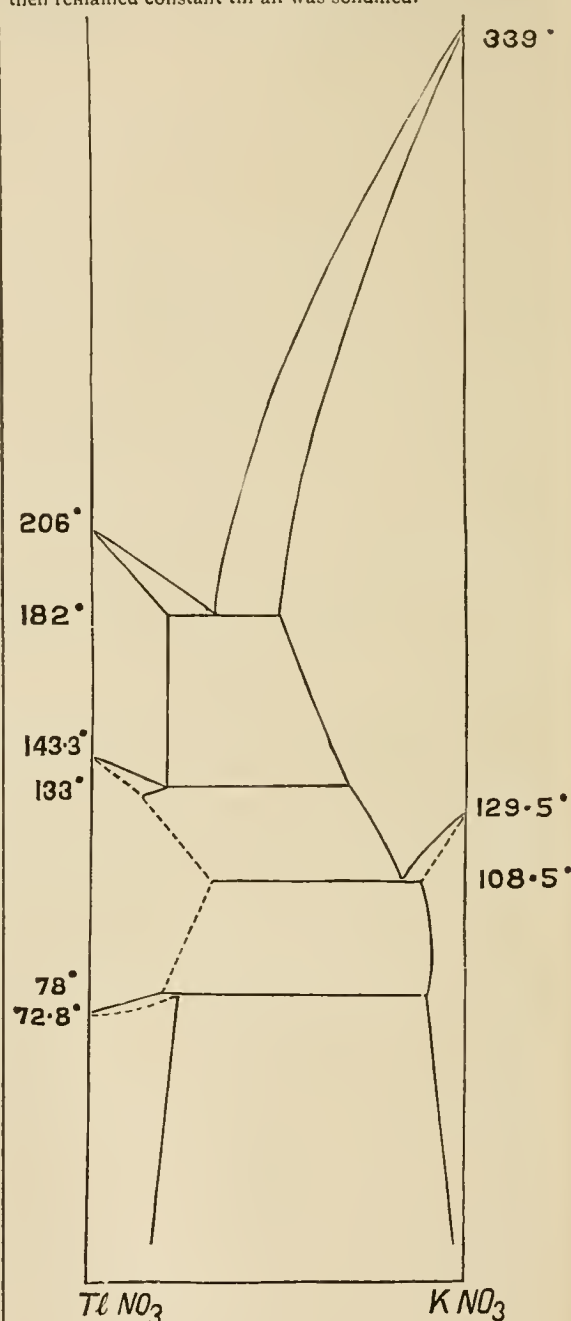


Fig. 1.

Thus in this case probably the formation of the double salt does not occur for some time; a eutectic mixture separates out, and for some minutes the temperature remains constant. Then the separation of the double salt begins, and the temperature rises to the solidification point.

The mixture with 50 mols. per cent AgNO_3 solidifies at 82.8° . The temperature remains constant until the whole mixture is solidified. The crystals which are deposited are different from the first two sorts.

In this mixture with 50 mols. per cent AgNO_3 also supercooling takes place. But as soon as crystals separate the temperature does not fall any more, but at once rises to 82.8° .

The solidification point of the double salt and the two eutectic points, double salt + AgNO_3 and double salt + TlNO_3 , thus lie in an almost horizontal line. The formation of the double salt may not occur at all. In this case, the eutectic point $\text{AgNO}_3 + \text{TlNO}_3$ is reached.

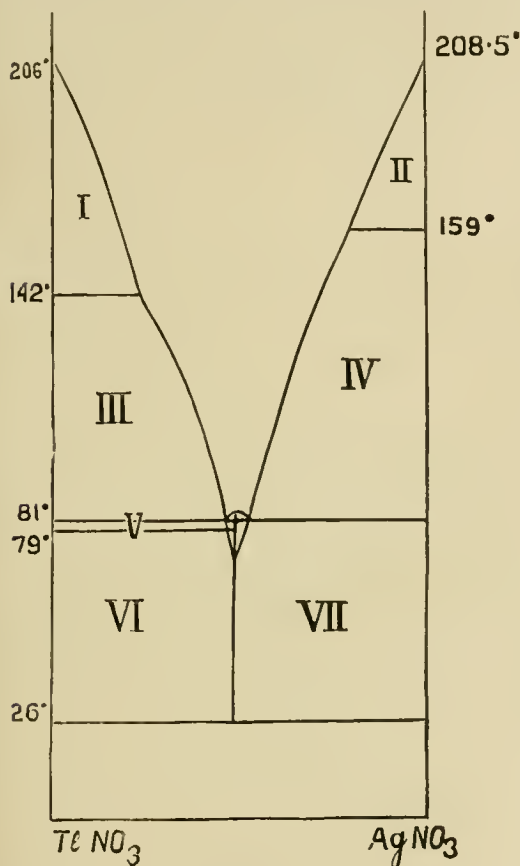


Fig. 2.

It was also frequently observed that the eutectic point was reached, but that the separation of the conglomerate ($\text{AgNO}_3 + \text{TlNO}_3$) only continued for some minutes, and afterwards the double salt was deposited while the temperature rose to 82.8° .

Since with TlNO_3 a transition occurs a little below 80° , it would be possible that the above mentioned heating effect has its cause in the transition of the TlNO_3 .

As was already mentioned in the case of the system $\text{KNO}_3 - \text{TlNO}_3$ the transition is easily greatly delayed, and the heating effect is small. Moreover, it has been observed that the temperature remained constant at 74.6° and at 82.8° , not only with mixtures with more than 50 mols. per cent TlNO_3 (thus after the solidification $\text{TlNO}_3 + \text{double salt}$), but also with mixtures with more than 50 mols. per cent AgNO_3 (thus after the solidification $\text{AgNO}_3 + \text{double salt}$). Thus in the latter case the heating effect cannot be ascribed to the transition of the TlNO_3 .

From the form of the solidification curve it follows that the crystals which are deposited from the melt of 0 to 48 mols. per cent AgNO_3 , and of 52 to 100 mols. per cent AgNO_3 , must either be pure TlNO_3 and pure AgNO_3 , or mixed crystals of these salts.

The fact that in mixtures containing large amounts of AgNO_3 and of TlNO_3 the end of the solidification can be observed at $\pm 80^\circ$ points to a small mixing, if any mixing at all takes place in the solid phase.

From the analysis of the crystals which are deposited from the melt it cannot be decided with certainty whether a slight mixing takes place, for it is not possible to obtain the crystals absolutely free from mother-liquor.

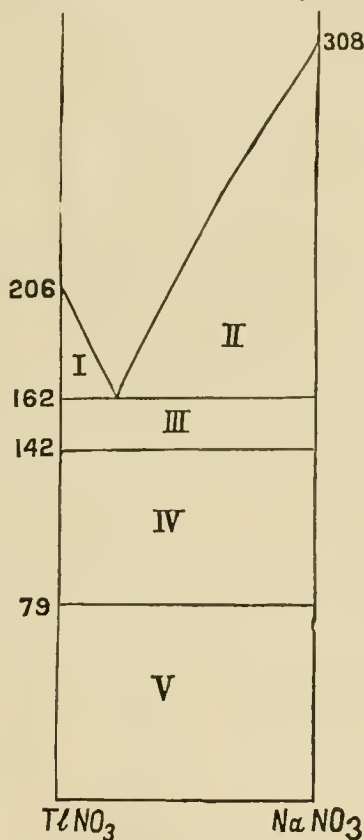


Fig. 3

An accurate criterion of the formation of mixed crystals is provided by the change in the transition temperature.

On the AgNO_3 side the rhombohedral crystals (thus pure AgNO_3 or mixed crystals) which are deposited from the melt are converted into rhombic crystals as the temperature falls, and this transition is revealed by a delay in the regular fall of the temperature. If pure AgNO_3 is deposited from the melt the transition takes place at 159° , and, if mixed crystals are deposited, at a higher or lower temperature than 159° .

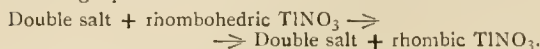
The same holds good for crystals which are deposited on the TlNO_3 side.

In the determination of the curve of solidification a lag was always observed in the neighbourhood of 159° with mixtures on the AgNO_3 side, which solidified at temperatures above 160° ; thus in mixtures with 100 up to ± 80 mols. per cent AgNO_3 .

On the TlNO_3 side the same occurs at 142° (regular—rhombohedral).

Thus from this fact it follows that neither on the AgNO_3 side nor on the TlNO_3 side are mixed crystals separated.

The solidified mixtures of different concentrations are thus conglomerates of the double salt with AgNO_3 (rhombic) or double salt with TlNO_3 (rhombohedral). The latter conglomerate is changed a 79° , according to the following equation:—



This transition of the TlNO_3 has been described above under the system $\text{KNO}_3\text{—TlNO}_3$. On continued lowering of the temperature a further transition takes place, which can be observed with the unaided eye, for as the temperature falls a white film forms over the solidified mixtures. But this transition takes place too slowly to allow of a determination of the transition temperature either by the optical or thermic methods; the dilatometric method was therefore employed. In order to show that the transition in these conglomerates is a transition which the double salt experiences and not the AgNO_3 or TlNO_3 , the following dilatometric experiments were performed:—

	I.	II.	III.
Temp.	Height of oil in dilatometer filled with pure TlNO_3 .	Height of oil in dilatometer filled with pure AgNO_3 .	Height of oil in dilatometer containing a mixture with 51 mols. per cent AgNO_3 .
36.6°	24.1	22.5	57.8
33.7	31.9	28.3	52.3
31	35.9	31.4	49.5
28.6	40.8	35	46.1

These three dilatometers were then cooled to 10° and kept at this temperature for about twenty hours, then again heated to 31° , and a reading taken to determine whether an alteration had taken place or not. It was then found:—

Temp.	I.	II.	III.
31°	35.9	31.4	34.4

Thus TlNO_3 and AgNO_3 remained unchanged while the volume of the mixture with 51 mols. per cent AgNO_3 became very much smaller. The transition temperature was now determined with different mixtures:—

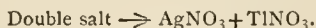
Increase in the height of the dilatometer with four mixtures with—				
Time in hours.	40 per cent AgNO_3 .	50 per cent AgNO_3 .	60 per cent AgNO_3 .	70 per cent AgNO_3 .
34.4°	4	+6.4	+6.9	+7.2
30.9	4	+1.4	+1.9	+1.3
27	6	+0.5	+0.8	+0.4
26	6	-0.35	-0.4	-0.2
24	3	-1.4	-1.4	-1.2
19	1	-1.4	-2	-1.8

For mixtures with 20 mols. per cent and with 80 mols. per cent AgNO_3 a transition-point was found between 24 and 29° . As it is the double salt which suffers the transition the transition temperature is all the more difficult to observe the less double salt the conglomerate contains. It is also probable that all mixtures are changed at the same temperature. It could be shown by solubility experiments which transition takes place. Two cases are possible:—

Either—



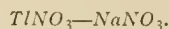
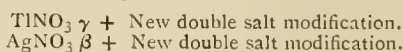
or—



In the different regions which are indicated in the figure we have the following phase complexes:—

- I. $\text{TlNO}_3 \alpha + \text{Melt}$.
- II. $\text{AgNO}_3 \alpha + \text{Melt}$.
- III. $\text{TlNO}_3 \beta + \text{Melt}$.
- IV. $\text{AgNO}_3 \beta + \text{Melt}$.
- V. $\text{TlNO}_3 \beta + \text{Double salt}$.
- VI. $\text{TlNO}_3 \gamma + \text{Double salt}$.
- VII. $\text{AgNO}_3 \beta + \text{Double salt}$.

The region below 26° the complex $\text{TlNO}_3 \gamma + \text{AgNO}_3 \beta$, or divided into two parts:—



Although it was established by preliminary experiments that in this system neither mixed crystals nor double salt were formed, and thus it was to be expected that the solidification curve would consist of two curves, which intersect in a eutectic point, while the transitions of the conglomerates of different concentration ($\text{TlNO}_3 + \text{NaNO}_3$) when the temperature falls would have to take place each time at the same temperature, nevertheless I determined the temperatures of solidification and of transition because, so far as I knew, an example of this simple case had not been worked out experimentally.

TlNO_3 , mols. per cent.	Temperature of solidification.
100	206.1°
98.1	203.5°
96	198.4°
84.7	176.4°
76.5	163.2°
71.7	174°
58.9	204.1°
46.5	228.2°
37.4	242.5°
25.1	263.7°
15.5	277.4°
0	308°

Thus, from the form of the curve of solidification, it follows that the crystals which are deposited from the melt must be either pure TlNO_3 and pure NaNO_3 or mixed crystals of these salts.

It would be expected in this case also that mixture in the solid phase is excluded, or would, at any rate, be small—as, for example, in the mixture with 95.9 mols. per cent TlNO_3 the end of the solidification can be observed at 163° .

As it is not possible to obtain the crystals quite free from mother-liquor, it can only be shown with certainty in the case of mixed crystals deposited on the TlNO_3 side that no mixed crystals at all are formed.

As was mentioned above in the system $\text{TlNO}_3\text{—AgNO}_3$, the formation of mixed crystals follows from the alteration of the transition-point of the TlNO_3 .

I have determined thermometrically the transition-point of the different mixtures with 100 per cent to 0 per cent TlNO_3 , and have found that the transition-point, TlNO_3 regular $\rightarrow$ TlNO_3 rhombohedral, is not altered by mixing with NaNO_3 .

As NaNO_3 is not polymorphic, it cannot be proved with certainty whether a very small mixing takes place in the solid phase.

Also the second transition-point of TlNO_3 , which has been observed optically, is not altered by mixing with NaNO_3 .

In the different regions which are shown in Fig. 3, we have the following phase complexes:—

- I. $\text{TlNO}_3 \alpha + \text{Melt}$.
- II. $\text{NaNO}_3 + \text{Melt}$.
- III. $\text{TlNO}_3 \alpha + \text{NaNO}_3$.
- IV. $\text{TlNO}_3 \beta + \text{NaNO}_3$.
- V. $\text{TlNO}_3 \gamma + \text{NaNO}_3$.

Summary.

This article gives a complete review of the phenomena of solidification and transition of all mixtures of TlNO_3 with KNO_3 , TlNO_3 with AgNO_3 , and TlNO_3 with NaNO_3 .—*Zeit. f. Physikal. Chem.*, 1905, li., 721.

ON THE RADIO-ACTIVE MINERALS.* (SUPPLEMENTARY NOTE).

By The Hon. R. J. STRUTT, F.R.S., Fellow of Trinity College, Cambridge.

IN a paper read before the Royal Society on February 28, 1905, I drew attention to the fact that all thorium minerals, so far as could be ascertained, appeared to contain uranium and radium. Since then, I have examined a number of additional minerals, in order to test the induction further. The result has been quite confirmatory of the original conclusion. I have, in this further investigation, contented myself with determining the thorium and radium, for it may now be considered proved that radium is a product of uranium, and it is much easier to establish the presence of radium by its emanation than to detect uranium by chemical analysis. The experimental methods explained in the former paper were employed. The results are as follows:—

Mineral.	Locality.	Thorium, oxide, per cent.	Radium, millionths of 1 per cent.
Thorite ..	Ceylon	61.0	1.00
Thorite ..	Brevig, Sweden ..	53.9	0.81
Monazite ..	Johannesberg .. .	5.94	1.06
Alvite ..	Raade Moss, Norway	4.95	1.81
Xenotime ..	Raade Moss, Norway	3.89	0.90
Monazite ..	North Carolina (a) ..	3.79	0.53
Monazite ..	Nigeria	2.98	3.78
Anerodite? ..	Ceylon	2.27	9.80
Monazite ..	Malay Straits .. .	1.53	4.02
Fergusonite ..	?	1.31	26.7
Malacone ..	Hitteroe, Norway ..	1.15	1.40
Allanite ..	Amherst Co., Virginia	0.492	1.08
Yttrotantalite	Ytterby, Sweden ..	0.437	5.56
Polycrase ..	?	0.334	0.36
Zircon ..	North Carolina .. .	0.307	0.34
Zircon ..	Virginia	0.217	0.52

(a) This consisted of pure grains of monazite, picked out from the commercial sand.

In conclusion, I must express my best thanks to several friends, especially Professor W. R. Dunstan, for specimens of these minerals, which would, in some cases, have been impossible to procure otherwise.

DETERMINATION OF SUGAR BY MEANS OF FEHLING'S SOLUTION.

By FRANCIS P. LAVALLE.

In determining the quantity of sugar in urine and other liquids containing sugar, it is frequently very difficult to observe the end of the reaction.

Cuprous oxide forms deposits very slowly, and its colour is reflected on the surface of the solution. The determination is the more difficult the smaller the quantities of sugar concerned. Even if the solutions containing sugar have been deprived of all colouring matter, yet in treating the liquid with Fehling's solution the fluid assumes a yellowish greenish colour and turns turbid, so that the end of the reaction cannot be recognised.

Now it is well known that Na, OH, and KOH with cupric salts yield a precipitate which is soluble in excess of the precipitants, when sugar or similar organic substances are present. Likewise cuprous oxide is soluble in an excess of alkalis, and I made use of this peculiarity to determine the sugar by means of Fehling's solution, to which an excess of alkalis had been added. In this manner the separation of cuprous oxide is avoided, and an entirely colourless liquid is obtained which at the most contains an unimportant sediment.

I proceed as follows:—Into a porcelain dish holding 200 c.c., I place 5 or 10 c.c. of Fehling's solution, 30 c.c. of caustic soda (1:3), and 50 or 60 c.c. distilled water, heat it, and when the fluid begins to boil I gradually add some of the solution of sugar whose percentage I wish to determine. The operation is finished as soon as the last drop causes the blue colour of Fehling's solution to disappear.

The controlling experiments which I have made after this method have been very satisfactory. I can therefore recommend this method on account of its simplicity and the little time it requires.

DETERMINATION OF NITRITES IN WATERS.

By W. P. MASON.

APROPOS of R. S. Weston's interesting notes upon this topic (*Journ. Am. Chem. Soc.*, xxvii., 281), it may be worth while to call attention to the fact that the "nitrite" error, due to the presence of burning Bunsen lamps, is often much greater than is suspected. In the water laboratory here the chemically pure distilled water is prepared by the use of a large copper retort heated by a very broad Bunsen burner. Only one other lighted burner is constantly in the room, and that a small one. Distilled water, as delivered by the tin worm, was tested with the following results, duplicates being run in each instance. One Nessler tube was exposed to the room atmosphere, after addition of the nitrite reagents, and the other carefully protected therefrom. The results are stated as parts per million.

Conditions under which distilled water was collected.	Nitrites present in protected tube.	Nitrites present in unprotected tube.
Not allowed to come in contact with air of laboratory	None	0.0015
Slight contact with air. Tin condensing tube entering neck of receiving bottle..	0.002	0.003
Water allowed to drop six inches through open air to receiving casserole..	0.007	0.008

—*Journal of the American Chemical Society*, xxvii., No. 5 May, 1905.

A COLOURED REACTION FOR COTTON-SEED OIL.

By G. HALPHEN.

IN the year 1897 (*Journ. de Ph. et de Chim.*) I described a reagent composed of equal volumes of amylic alcohol and sulphide of carbon having 1 per cent of sulphur in solution, which, when heated on the water-bath, or better still on a salt-water bath, with cotton-seed oil or substances containing it, gives rise to a characteristic red colouration.* At the same time I showed that the active principle, the cause of the colour, accompanied the "liquid" or non-saturated acids when they were separated from the oil. But, in spite of numerous attempts, I have not been able, up to the present, to separate this substance which appears to be present in the oil in very small quantities.

With the object of elucidating the mechanism of this reaction, Raikow (*Chemiker Zeit.*, 1900, pp. 562 and 583) submitted cotton-seed oil to oxidation by means of permanganate in sulphuric solution, and he observed that, after a certain degree of oxidation, the oil lost the property of reacting on the above mentioned reagent.

* Since that time a new oil called oil of Kapok has been discovered, which appears to belong to the same family, and which also gives this reaction.

* A Paper read before the Royal Society, June 8, 1905.

From this he concluded that we really have to deal with a non-saturated acid possessing the property of fixing sulphur and giving rise to sulphurised aldehydes or ketones.

It appeared to me necessary to determine in a more exact manner the nature of the active substance, for Raikow's experiment did not seem to be conclusive.

For if we can really saturate the incomplete acids by means of permanganate of potash, the action of the reagent may, at the same time, profoundly modify or even destroy other substances which, saturated or not, may, however, be looked upon as being the cause of the red colouration.

For the purpose of deciding this point I saturated the glycerides of cotton-seed oil by carefully acting with bromine in sulphocarbonic solution until there was a distinct excess. The excess of the halogen was removed by agitation or by a solution of sulphite of soda or phenol, and the solvent eliminated by spontaneous evaporation. Under these conditions the bromised derivatives are seen to be incapable of producing the red colouration.

On the other hand, cotton-seed oil which had been turned red through the action of amylic alcohol and sulphurised sulphide of carbon, was bromised under exactly the same conditions as above. After the elimination of the solvent there remained a red oil, having practically the same colour, but with the addition of a brownish tint.

Finally, the cotton-seed oil was saponified, and the soap exhausted with petroleum ether to extract the non-acid or unsaponifiable substances. The petroleum ether, well washed with alcohol diluted to 50°, deposited a residue which was proved to be incapable of giving a red colouration; consequently it appeared very probable that the active substance has the double character of an acid and a non-saturated acid.

The hypothesis of the formation of thio-derivatives in the manner proposed by Raikow is less surely established.

I have, in fact, proved that the presence of the sulphide of carbon is indispensable; without it there is no red colouration, neither by heating the oil direct with sulphur, nor by heating the same oil with sulphur in the presence of solvents such as amylic alcohol, or benzene for example.

Raikow himself has shown that when we assist the action of sulphur or sulphide of carbon on cotton-seed oil, by means of light, in the absence of amylic alcohol, the red colour is not only not produced, but that it is no longer susceptible of being produced. Now, if we remember that I pointed out that amylic alcohol only helps to accelerate the reaction, we are brought to the conclusion that we have to do with a reaction which may give rise to different products, according to the conditions of the experiment.

From another point of view, based on the observation that light acting on red cotton-seed oil decolours it,* Raikow puts forward the opinion that, in the light, these sulphurised compounds lose sulphur, forming products of polymerisation, in the same way that stilbene is produced at the expense of thiobenzaldehyde. But then we must admit that water also must have this polymerising property. If, in fact, we introduce at the same time as the oil and the reagent one-third the amount of water, for instance, no red colouration is produced, even when the heating is prolonged for an hour; on the other hand, a slight orange-brown tint appears, which shows that there is a modification of the reaction.

Oil treated in this manner, although carefully separated from the accompanying water, is no longer capable of giving the red colouration, and it is necessary to draw the special attention of analysts to this peculiarity that has not been observed before.

Now, water either alone or charged with aldehydes is without action on the active principle. We can furnish

* I found it impossible to obtain complete decolouration by this means. Reddened oil exposed for three years to broad daylight and in a closed vessel, became black and lowered in tone without giving the complete decolouration that this chemist obtained in a much shorter time.

the proof by heating cotton-seed oil with these substances, then extracting with petroleum ether and evaporating the solvent. The residue which has undergone the action of water and aldehyde, possesses, from the point of view of developing the red colouration, the same qualities as the original oil. Similar results to these have been obtained with oil of Kapok.

But this polymerising action of water is far from being properly established, for I have shown that as soon as the red colouration is produced, it resists the action of the water.

It must be further noted that in the reaction of sulphurised sulphide of carbon on oil of cotton-seed, sulphuretted hydrogen is given off (Raikow, *loc. cit.*), and that the production of this body is greater in the presence of amylic alcohol than in its absence, which would appear to establish a connection between the development of the red colouration and the production of sulphuretted hydrogen. I would remark here that in all cases traces of water or of oxyhydril groups may produce sulphuretted hydrogen by reaction on the CS₂. Now the thiols are produced precisely by the action of the sulphuretted hydrogen on the aldehydes in the presence of water. I have attempted to find out whether the red colouration was due to the action of this sulphuretted hydrogen, by making it react on cotton-seed oil either alone or in the presence of water, amylic alcohol, or sulphide of carbon; in no case did I observe any red colouration. We are right, therefore, in concluding that the second part of Raikow's hypothesis is not justified by experience.—*Bull. Soc. Chim.*, Series 3, vol. xxxiii., No. 1.

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY.

CONVERSAZIONE AT BURLINGTON HOUSE.

ON Friday evening last, the 23rd inst., the annual Ladies' Soirée was held at the Society's Rooms, at Burlington House, the Fellows and guests being received by Sir William and Lady Huggins and Members of the Council. The enjoyment of the evening was enhanced by a number of interesting exhibits, some of which, however, had been shown already at the previous *Conversazione* in May.

Among the fresh ones which attracted most attention we come first to that of Mr. G. T. BEILEY, who showed a very fine specimen of the metal Sodium, prepared so as to show its true colour and lustre. The specimen was prepared by Dr. Thomas Ewan by melting the metal *in vacuo* in one vessel and running the clean, bright part of the liquid into another communicating vessel which had been freed from condensed air or moisture by heating during exhaustion. After solidification of a crystalline crust, the surplus liquid was run back into the first vessel and the specimen globe was sealed off.

THE GENERAL ELECTRIC COMPANY exhibited the "Osmi" Incandescent Lamp. The lamp in appearance is similar to the ordinary electric bulb, but in place of carbon the filament is made from the rare metal osmium, which when in a state of incandescence glows with extreme brilliancy. The advantages claimed are:—High fusing point, white light, higher electrical efficiency, longer life, saving of current, less heat. The blackening of bulbs is unappreciable. Consumption of current with ordinary carbon filament lamp, 3·5 to 4 watts per C.P. Consumption of current with Osmi lamp, 1·5 watts per C.P.

MESSRS. SIEMENS BROS. & Co., Limited, exhibited specimens of Tantalum and Tantalum Lamps. 1. The metal tantalum in the form of small blocks of more or less purity, also of sheet and of metallic powder, and specimens of wire of various thicknesses, 2. A series of tantalum

glow lamps, requiring 110 volts and 0.54 ampère to give a light of 25 N.C. ($1\frac{1}{2}$ watts per candle power).

In the Council Room Mr. W. SHACKLETON, F.R.A.S., showed a Mechanical Lantern Slide illustrative of the phenomenon of a total Solar Eclipse. A white disc representing the sun is projected on the screen; by moving an opaque disc representing the moon, this is gradually obscured, and the preliminary partial phases of a total solar eclipse are shown. A moment before complete obscuration a twin shutter is opened, which allows the corona and chromosphere to be projected, thus reproducing totality, which may last as long as desired. A further movement of the black disc reveals the crescent sun again, when the shutter is closed and the corona obliterated. Continuing the movement, the final partial phases are shown, terminating with the sun shining as at first.

Sir WILLIAM CROOKES, F.R.S., exhibited Stereoscopic Photographs of the recently found "Cullinan" Diamond, of Diamonds in the Diamond Office, Kimberley, and of other large Diamonds.

The MARINE BIOLOGICAL ASSOCIATION had an interesting exhibit of Living Representatives of the Plymouth Marine Fauna.

Mr. T. E. HEATH showed a number of excellent stereoscopic views of the Sun and Stars of estimated parallax.

No. 1.—Distance from sun, 300 light-years; looks towards 90th° of North Declination.

Nos. 2 to 5.—All 150 light-years from sun: No. 2 looks towards VI. hour of R.A.; No. 3 towards XII. hour; No. 4 towards XVIII. hour; No. 5 towards XXIV. hour;

No. 6.—Distance from sun, 100 light-years, looks towards 90th° of South Declination.

The perspective drawings are made from a plan and elevations in which the scale of stellar distances is to light-years to one inch, and of stellar discs such that the sun (or a star which gives equal light is $\frac{1}{8}$ th of an inch in diameter. Magnitudes vary with the varying distance of the spectator.

The Star discs are perforated and covered by coloured films so that they shine thus:—Orion Stars, greenish; Sirian, bluish white; Procyon, pale yellow; Solar, yellow; Antarian, reddish.

Mr. C. BAKER, showed the Etlles-Curties Ophthalmometer and Ophthalmic Microscope. The ophthalmometer is an instrument for measuring the radius of curvature of the cornea, and consequently of ascertaining the dioptric value of the refracting medium bounded by that curvature.

A very interesting exhibit was that of Dr. ALBERT A. GREY; it consisted of specimens of the Membranous Labyrinth of Man and some Animals. Membranous labyrinths of man, illustrating normal and pathological conditions. The membranous labyrinth of the seal showing otoliths. The membranous labyrinths of the mouse, the rat, the rabbit, the sheep, the cat, the lemur, the duck, the hen. The brain of the haddock, with the otoliths in their natural position.

Dr. W. J. RUSSELL, F.R.S., exhibited:—

1. Pictures produced in the *dark* on a photographic plate by different woods.

2. Ordinary photographs of the same woods.

3. The woods used in the experiments.

The pictures taken in the *dark* were obtained on an ordinary rapid photographic plate, the wood being in contact with the plate from 1 to 18 hours at a temperature of 55° C. The pictures were developed in the same way as if they had been produced by light.

Sir W. H. PREECE, K.C.B., F.R.S., showed a New Sundial that tells Standard Time; designed by Professor Albert Crehore. The gnomon of the common form of dial is abandoned and the shadow of a small bead fixed on a wire is cast on the interior of a true cylindrical surface upon which figure-of-eight curves are drawn marking

standard noon for each day of the year. The cylindrical surface is inclined so that its axis, upon which the bead is fixed, is parallel to that of the earth. It thus represents the latitude of the place. The shadow of the bead travels across the cylindrical surface parallel to, or on one of the circles drawn thereon. These circles represent days of the months. Each hour described in the circle is always of the same length, and a scale of minutes engraved on the cylinder enables true mean time to be read off directly to a few seconds.

During the evening three demonstrations were given in the Meeting Room with lantern illustrations:—

Dr. EDWARD A. WILSON. Views of the Antarctic. The slides comprise general views of the life and work done on board the "Discovery" during the years 1902 to 1904, and views of the seals, penguins, and other birds met with in the Antarctic circle.

Sir W. de W. ABNEY, K.C.B., F.R.S. Lantern Slides of the Three-colour Process. The photographs in colour shown are prints from three negatives for each subject taken. Each of the three negatives is taken through an appropriate coloured medium, and the three transparent prints are projected on a screen with appropriate coloured screens behind them, giving the colours of Nature. The process and apparatus employed is based on that of Mr. Ives.

Prof. E. B. POULTON, F.R.S. Recent work in Mimicry and Protective Resemblance.

PHYSICAL SOCIETY.

Ordinary Meeting, June 16th, 1905.

Prof. J. H. POYNTING, F.R.S., President, in the Chair.

A PAPER "On the Ratio between the Mean Spherical and the Mean Horizontal Candle-power of Incandescent Lamps" was read by Prof. FLEMING.

This paper contains a theoretical deduction from first principles of experimental results given by Mr. G. B. Dyke, B.Sc., in a paper read before the Physical Society on November 11th, 1904, respecting the ratio of the M.S.C.P. of incandescent electric lamps to the M.H.C.P. taken when the lamp was rotating round a vertical axis. In the case of nine different types of electric glow-lamps, this ratio was found to be a number near 0.78. The author shows, by discussing the simple case of a linear filament, that the ratio of the M.S.C.P. to the horizontal candle-power for this last case must be represented by the value $\pi/4 = 0.785$, and hence that the constant ratio found experimentally by Mr. Dyke necessarily follows as a simple consequence of the fact that the light sent out in any direction from each unit of length of an incandescent filament varies as the cosine of the angle of inclination of the ray to the normal to the filament. In the paper it is shown also how a simple correcting factor may be obtained for reducing the actual horizontal candle-power of a linear filament of finite length to the candle-power in the same direction which would be found if the elements of the filament were concentrated on the axis of the photometer and all normal to it. If ϕ is the angle subtended by any linear filament at the photometer-disc, then the expression $\frac{1}{2}[\cos \phi + \phi \cot \phi]$ is the correcting factor which must be applied to correct the candle-power of the filament in the sense indicated above. From this expression is derived a general expression for the ratio of the mean spherical to the mean horizontal candle-power of a filament of finite length when the measurements are made at such a distance that the length of the filament subtends a sensible angle at the photometer. The results of experiments are also described, justifying the assumption of the above cosine law of radiation.

Mr. G. B. DYKE briefly described the experiments which had been performed to justify the law.

Mr. L. GASTER thought that the subject discussed by Prof. Fleming deserved considerable attention at the hands of lamp manufacturers. Owing to the improvements made in recent years in the manufacture of incandescent lamps it is advisable, in comparing their relative merits, to consider the mean spherical candle-power given out, and to determine the total flux of light per watt consumed, thereby conveying an accurate meaning as to the efficiency of the lamp as an energy transforming device.

Dr. CHREE pointed out that the quantity $\frac{1}{2}(\cos^2 \phi + \phi \cot \phi)$ was based on a calculation which supposed the photometer-disc exactly opposite an end of the filament and required modification when this was not the case. When D/l was so large that ϕ was small, higher powers of ϕ being neglected, the quantity reduced to $1 - \frac{3}{2}\phi^2$; but if the photometer-disc were opposite the centre of the filament ϕ had to be replaced by $\phi/2$ and the departure of the quantity from unity was reduced to a quarter. He remarked that the quantity $\frac{1}{2}(\cos^2 \phi + \phi \cot \phi)$ had to be applied as a *divisor* to the observed illumination to deduce what the result would be under the ideal conditions when D/l was so large that ϕ was negligible; and he was doubtful whether the language employed, especially the description of the quantity as a "correcting factor," was sufficiently free from ambiguity.

Prof. J. A. FLEMING said he had tried to impress upon lamp users the advantages of expressing candle-power in terms of the total flux of light per watt consumed. Now that a simple relation had been established between M.S.C.P. and M.H.C.P., there was no excuse for expressing the candle-power of a lamp as its *maximum* horizontal candle-power.

Dr. H. A. WILSON read a paper on "*The Electrical Conductivity of Flames.*"

The paper contains an account of a series of experiments on the conductivity of a coal-gas flame for electricity between platinum electrodes immersed in the flame. The variation of the current with the distance between the electrodes and the fall of potential along the flame are investigated by using a special burner producing a long narrow flame. The burner consists of a fused quartz tube with a series of small holes parallel to its diameter. The electrodes are two parallel discs of platinum, one fixed at one end of the flame, and the other capable of movement horizontally in the flame, so that it can be placed at any desired distance from the fixed electrode. The current through the flame was measured by a moving coil galvanometer, and the potential difference between the electrodes by an electrostatic voltmeter. The quartz-tube burner being a good insulator enables a current to be passed from one end of the flame to the other without fear of any of it going through the tube instead of through the flame. It thus enables the effect of putting salts into different parts of the flame to be easily studied.

Dr. J. A. FLEMING said that the paper was of practical interest, and described some experiments he had made to utilise the properties of flames rendered conducting by potassium salts in the construction of a sensitive telegraphic relay.

Mr. W. DUDELL drew attention to the similarity of the phenomena described to those exhibited by electric arcs. He asked the author if he had considered the possibility of using a conducting flame as a high voltage rectifier. Also had the author tried sodium salts, and what were their effects compared with those of potassium.

Dr. W. WATSON asked if the drop of potential at the negative electrode depended upon the temperature of the electrodes.

Dr. H. A. WILSON, in reply to Mr. Duddell, said that the salts of caesium, rubidium, potassium, sodium, and lithium imparted conductivity to flames in the order named. This order was also the order of the atomic

weights. He had found that a flame could be used as a rectifier when using alternations about 100 $\sim$ per second, but was not sure whether it would rectify rapidly alternating currents. In reply to Dr. Watson, he said that the temperature of the electrodes exercised a great influence. An increase in the temperature of the electrode diminished the drop of potential at the electrode.

A paper on "*Contact with Dielectrics*" was read by Mr. ROLLO APPEYARD.

The object of the paper is to examine—

1. Whether tin-foil electrodes, pressed against a sheet of dielectric by india-rubber disks, enable accurate determinations of dielectric-resistance to be made.

2. The effect upon dielectric-resistance of change of load on such tin-foil electrodes, in the case of press-spahn.

3. The effect upon dielectric-resistance of increase or decrease of voltage in the case of press-spahn between tin-foil electrodes.

4. The rate and direction of the change of deflexion in direct-deflexion tests on press-spahn, and to determine in how far these changes result from surface conditions, and in how far from internal stresses.

5. The effect of reversals of voltage upon dielectric-resistance.

6. The effect of prolonged "electrification."

7. To indicate the probable limits of accuracy with mercury electrodes.

8. To point out that Price's guard-wire can be used in sheet tests to eliminate leakage over the sheet surface, as well as over the instruments.

Among the conclusions arrived at are the following:—

- a. Except in the case of homogeneous dielectrics, it is misleading to deduce specific values referred to unit cube of the material, from the results of tests on sheets.

- b. With tin-foil electrodes, the apparent resistance or press-spahn diminishes as the load increases, and it attains a fairly constant value at a load of 400 grms. per c.m.²

- c. If with tin-foil electrodes, the load is gradually diminished after a load of 543 grms. per c.m.², the resistance gradually rises, but the rise is less rapid than the diminution in the former case (b).

- d. When the full load with tin-foil electrodes is again restored the resistance falls to its minimum value.

- e. For small loads, with tin-foil electrodes, the 2nd-minute deflexion is in general greater than the 1st-minute deflexion. As the load increases, a point is reached at which these deflexions become approximately equal. For loads greater than about 360 grms. per cm.², the 1st-minute deflexion is in general greater than the 2nd-minute deflexion.

- f. Increase of voltage, with tin-foil electrodes, especially with small loads, behaves like increase of load, apparently increasing the contact area, and diminishing the observed dielectric resistance. Load, voltage, and the normal effect of "absorption" thus combine to determine the ratio of the 1st-minute deflexion to the 2nd-minute deflexion.

- g. When mercury electrodes are used, the dielectric-resistance, as measured at different voltages, is sensibly the same, even for abrupt and great changes of voltage.

- h. When mercury electrodes are used, the 2nd-minute deflexion is in general never greater than the 1st-minute deflexion. The inference is that when, with tin-foil electrodes, the converse is the case, it arises from imperfect contact, and not from the material itself.

- i. When mercury electrodes are used, the dielectric-resistance, as measured with a voltage applied in a given direction, is sensibly the same as that measured with the voltage reversed, and this equality appears to become greater after a few reversals.

- j. There is a critical load at which tin-foil electrodes yield fairly accurate results. With greater loads there is danger of crushing the material. With a less load the contact is faulty.

Mr. DAVID OWEN, in reference to the variation of apparent resistance with the volts applied in the case of

the experiments made by the author where tin-foil electrodes were used, pointed out that an effect of the same kind takes place in the case of the leakage resistance of condensers of paraffined paper and tin-foil. If the insulation resistance be measured by observing the rate of leak of the condenser, the curve of volts and time drops more slowly than according to the exponential law. The same result is obtained if the current maintained by the application of a steady voltage across the condenser terminals is measured by a galvanometer in series. For such a condenser a recent test gave an apparent resistance of 100 megohms for a P.D. of 4 volts, but this value steadily dropped with rise of voltage and was 41 megohms for 20 volts. Though the voltage here used was much less than those applied by the author, the effect in question is the same in kind and in degree.

Mr. A. CAMPBELL said Mr. Appleyard's paper was an interesting contribution to our knowledge of a difficult but practically important subject. He had established the advantages of mercury electrodes. Mr. Campbell remarked that he had used tin-foil and indiarubber electrodes for the last fifteen years, and mentioned that before they were adopted at the National Physical Laboratory for Mr. Rayner's and other work, they were put through a series of tests with varying weights, and from the observations a working pressure was chosen which gave tolerably accurate results. He had also tried guard-wires with several kinds of sheets, and found that the surface leakage was negligible. In Mr. Rayner's experiments at high temperatures, the changes due to a fall of temperature of a few degrees were so enormous that any inaccuracy due to the clamps was of trifling importance. Mr. Campbell mentioned that when measuring the capacities of thin sheets, tin-foil electrodes gave results which in some cases varied with the applied pressure. For example, with dry paper as dielectric, increase of pressure gave considerable increase of capacity, and since in this case the contact does not matter, the effect must have been due to approach of the electrodes. If the paper be black-leaded the change of pressure has less effect. He therefore suggested that in cases where mercury was inconvenient, the use of black-lead might be of advantage.

Dr. H. A. WILSON expressed the opinion that when using mercury electrodes the diminution in resistance might be due to compression of the dielectric caused by the pressure of the mercury, rather than to better contact between the mercury and the dielectric.

Mr. W. A. PRICE said that the question of insulation tests was an important and far-reaching one. Dr. Wilson had suggested that the pressure of the mercury might cause a change of form, but he did not think that pressures so small would produce any appreciable change. The author had shown that provided you obtained good contact between the electrodes and the dielectric, you could obtain constant values for the insulation resistance.

Prof. W. CASSIE suggested that the pressure might be applied to the tin-foil electrodes by placing a sheet of indiarubber over each of them, or by putting the plate of dielectric with its tin-foil electrodes in a flat indiarubber bag and pumping out the air under the indiarubber. Thus the pressure of the atmosphere would produce more uniform and effective contact of the tin-foil with the dielectric. The pressure obtainable in this way might have any desired value up to about a kilogram. per square centimetre.

Mr. R. APPELYARD, in reply to Mr. Campbell's suggestion with regard to the use of black-lead, pointed out that it was necessary to guard against moisture. Spurious effects might be introduced by electrolytic action.

The following papers were taken as read:—

"The Pendulum Accelerometer; an Instrument for the Direct Measurement and Recording of Acceleration," By Mr. F. LANCHESTER.

"A New Form of Pyknometer." By Mr. N. V. STANFORD.

Mr. ROLLO APPELYARD exhibited a Refractometer for the determination of refractive indices which can be used as an ordinary spectrometer, as an Abbe refractometer, or as a Pulfrich refractometer.

NOTICES OF BOOKS

Forty-first Annual Report on Alkali, &c., Works. By THE CHIEF INSPECTOR. London: Eyre and Spottiswoode. 1905. Pp. 155.

THE present Report deals with the proceedings during the year 1904.

There are now 1040 works in England, Ireland, and Wales registered under the Acts. Of these, 73 only are works decomposing salt, and so scheduled as alkali works; while the remainder, 967, carry on processes which are scheduled—or subject to registration—under the Acts of 1881 and 1892. There are 133 works registered in Scotland, bringing the total number of works registered in the United Kingdom to 1173. During the year 5053 visits were made by Inspectors, who carried out 4808 tests, and it is satisfactory to note that no proceedings have been taken during the year, for the recovery of penalties for infraction of the limit clauses regulating the amount or intensity of acid escapes, or for failure to use the best practicable means for the prevention of the escape of noxious or offensive gases.

The number of chlorine works in active operation in 1904 is less than before, as the bleaching powder industry has not recovered from the depression caused by the events of 1903.

In a total world production of 260,000 tons of bleaching powder one-half is produced by electrolytic methods, the other half by methods in which muriatic acid, liquid or gaseous, is the source of chlorine.

In the table given on page 8, it is seen that there is remarkably little variation between the average figures of escape in any of the nine districts in the manufacture of sulphuric acid. These figures vary from 1.42 to 1.04, the limit hitherto allowed being 4 grains of sulphuric anhydride per cubic foot of gases escaping from the exit of the process.

The attention of manufacturers continues to be given to various additions to and modifications in plant, designed to still further improve conditions and opportunities for yet more rapid and perfect reaction among the various constituents of the chamber gases.

Though the number of chemical manure works has shown a steady reduction during the last three years, the operations in the larger works tend to increase year by year, as indicated by the increased importation of mineral phosphates.

Sulphate and muriate of ammonia and gas-liquor works still continue to increase in numbers, such works forming by far the largest contribution to the total, viz., 484, or 33.3 per cent. In January of the present year there was a sad fatality, involving the loss of two lives, at the Corporation Gas Works at Batley; a short account of the circumstances and the verdict of the coroner's jury is given on p. 100.

The recovery and production of ammonia, as shown by the amount of sulphate of ammonia produced in the United Kingdom, still shows an increase, and it appears likely that the rate of extension in 1905 will be even greater. The inspectors are to be congratulated on their success in carrying out not only their administrative duties, but also the experimental work in their endeavours to still further diminish the escape of noxious gases from these processes.

White Phosphorus Liberated from Phosphorus Sulphide.—Léo Vignon.—The author analyses commercial phosphorus sulphide, as used in the manufacture of matches. He finds that, using Mitscherlich's method, the presence of phosphorus cannot be detected, but the latter substance can be identified by the action of a current of hydrogen.—*Comptes Rendus*, cxli., No. 22.

CORRESPONDENCE.

ACETYL DERIVATIVES OF STARCH.

To the Editor of the Chemical News.

SIR,—In the *Chemiker Zeitung* (May 17) Cross, Bevan, and Traquair announce the preparation of low acetyl derivatives of starch which have the physical characteristics of gelatin. These presumably contain no nitrogen, and, in view of the supposition that nitrogen is necessary to bacteria culture, it would be interesting to investigate the action of bacteria (and also of enzymes) on them.

This might lead to a method of distinguishing different types of microbes. One could add known amounts of nitrogenous matter in various forms and note the effect.

Mr. Burke's experiments on bouillon suggest the use of radium on these artificial gelatins.

With regard to the question of Life, there seems to me to be some confusion of thought about the power of reproduction. Reproduction, though we use it as a test for life, is not an essential characteristic of it. Life is conceivable without the power of reproduction. The formation of crystals may be due to such life. In other words, there may be different degrees of life.—I am, &c.,

H. H. S.

June 20, 1905.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

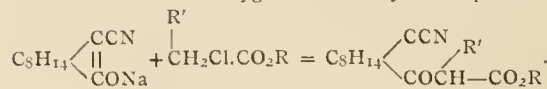
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxl., No. 22, May 29, 1905.

Cyanocamphacetic, Cyanocampho- α -propionic, and Cyanocampho- α -isobutyric Acids and their principal Derivatives.—A. Haller and A. Couréménos.—Cyanosodo- and cyanopotasso-camphors behave towards alcoholic iodides in the same manner as enolic bodies,

giving ethers of the form $C_8H_{14} \begin{array}{c} \diagup C-CN \\ \diagdown \quad \parallel \\ \quad \quad COR \end{array}$. These ethers,

under the influence of hydrochloric acid, are converted into the alcoholic chlorides and cyanocamphor. When the monochloracetic, α -monobromopropionic, and α -bromoisobutyric ethers are substituted for the alcoholic iodides, compounds are obtained in which part of the acid molecule is united with the oxygen of the cyanocamphor:—



These compounds split up under the influence of hydrochloric acid into cyanocamphor and probably the primitive halogen acids.

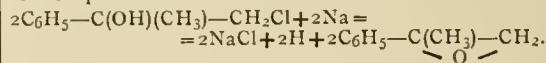
A Reaction of Green Chromic Sulphate.—Albert Colson.—The isomerism of the violet and green sulphate of chromium being established, the author finds—in the green salt—that the acid is less energetically fixed on to the chromium than in the violet salt. This discovery seems to indicate the fact that the decomposition of the green sulphate is easy. He finds, however, that, in reality, it is irregular, and his experiments lead to an investigation of one aspect of the question of dissimulated radicles, and the fact is discovered that the dissimulation of a radicle is closely connected with the velocity of reactions.

Physical Properties of Propane.—Paul Lebeau.—Propane boils at -44.5° . The critical temperature is 97.5° , and the critical pressure 45 atmospheres. These numbers

are very near to the results previously obtained by Olszewski. Propane is soluble in a large number of reagents, and this solubility is greater than in the case of methane and ethane. Finally, propane is still liquid at -195° . The author also finds that the pure ethane prepared by his method is also liquid at this temperature. Methane, the first term of this series of saturated carbides, solidifies and crystallises at -184° .

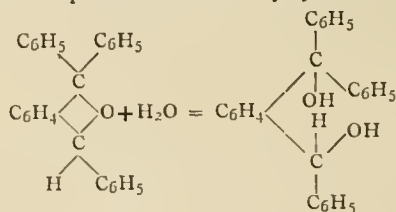
Methylacetylcarbinol.—André Kling.—The author finds that methylacetylcarbinol, which is a secondary ketonic alcohol, possesses general reactions comparable with those of acetol and propionylcarbinol.

Metho-ethenyl Benzene Oxide (Methylstyrolene).—M. Tiffeneau.—The oxide of metho-ethenyl benzene is prepared by the action of metallic sodium on the ethereal solution of methoethenyl benzene chlorohydrine according to the equation—

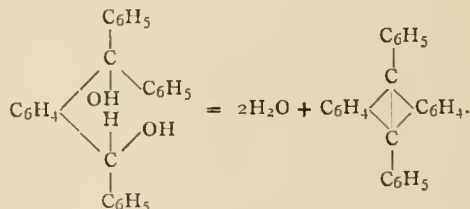


This oxide boils at $84-86^\circ$ at 15 m.m. pressure; its density is 1.043 at 0° . When distilled at ordinary pressure it boils at $190-200^\circ$, being almost completely transformed into hydratropic aldehyde. Dilute acids and sulphur bisulphite produce the same change.

Syntheses in the Anthracene Series. Condensation of the Benzodihydrofurfurane Derivatives into the γ -Substituted Anthracene Derivatives.—A. Guyot and J. Catel.—Continuing their researches on the benzodihydrofurfurane derivatives, the authors observe that these compounds condense very easily under the influence of strong sulphuric acid into the γ -substituted derivatives of anthracene and its hydride. The mechanism of this condensation can be explained very easily. A molecule of water is first fixed under the influence of the strong sulphuric acid, with rupture of the furfuran radicle and formation of a product of intermediary hydration,—



which condenses, forming an anthracene derivative,—



Methylnataloemodine and Nataloemodine.—E. Léger.—The author prepares and examines the properties of two anthraquinonic compounds found in Natal aloes.

Acidity of Commercial Ethylic Alcohols, and their Variations at Ordinary Temperatures.—René Duchemin and Jacques Dourlen.—The authors find that, at ordinary temperatures, alcohol is slowly oxidised in contact with air until acetic acid can be detected.

Conductivity of Colloid Solutions.—J. Duclaux.—The conductivity of colloidal solutions, though very slight, is not negligible. It is small if compared with the total mass of the colloid. The author proves that a very small portion of the mass is active, i.e., takes part in chemical reactions.

MISCELLANEOUS.

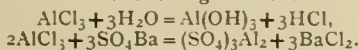
The Preparation of Two Ferrisodic Sulphates.—Anton Skrabal.— $2\text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 7\text{H}_2\text{O}$.—Heat on the water-bath 50 grms. of ferric sulphate dissolved with 10 c.c. of 10 per cent sulphuric acid and 300 grms. of Glauber salts. The dark colour due to the decomposition of the ferric sulphate disappears gradually, and gives place to a lighter colouration, and at the same time a yellowish white precipitate appears; the salt is a double one. This microcrystalline salt may be expected to have the formula

$$\text{Fe} \begin{pmatrix} \text{SO}_4\text{Na} \\ \text{SO}_4\text{Na} + 3\text{H}_2\text{O} \end{pmatrix} (\text{OH})$$

decomposition. $3\text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 6\text{SO}_3 \cdot 6\text{H}_2\text{O}$.—Heat 100 grms. of Glauber salts on the water-bath to aqueous fusion, then add a solution containing 10 grms. of ferric sulphate and 15 c.c. of concentrated sulphuric acid. By prolonged heating the salt is precipitated in the form of a white microcrystalline powder. Its probable constitution is $\text{Fe} \begin{pmatrix} (\text{SO}_4\text{Na})_3 + 3\text{H}_2\text{O} \end{pmatrix}$. Two double salts of the same composition have been already found in nature (Raimondi, "Minerals of Peru"; Tschermaks, *Zeit. f. Kr.*, 1891, vol. xviii., p. 595; and *Am. Journ. Sci.*, 1889, [3], vol. xxxviii., p. 244).—*Zeit. Anorg. Chem.*, vol. xxxviii., p. 318.

The Electrolytic Separation of the Alkaline Earthy Metals.—A. Coehn and W. Kettembeil.—The alkaline earthy metals can be separated one from the other by electrolyzing their solutions, using cathodes of mercury. The electromotive force necessary for the separation of the different metals (in the form of amalgams) varies by several tenths of a volt, so that by regulating the voltage in a suitable manner the separation is easy. The authors have obtained good results, for example, by electrolyzing the mixed solutions of chloride of barium and strontium, as well as the mixtures Ba—Ca and Sr—Ca. With saturated solutions, for example, the difference of potential observed for the formation of amalgam is from 0.2 volt for Ba/Ca, 0.25 volt for Sr/Ca, to 0.45 volt for Ba/Ca. As the solubilities of these three salts, BaCl_2 , CaCl_2 , and SrCl_2 , are very different, solutions of the same concentration show differences still more accentuated when we attempt to separate the metal electrolytically. The separation of Ba and Mg appears also to be possible by electrolysis.—*Zeit. Anorg. Chem.*, vol. xxxviii., p. 198.

A Method of Hardening Sulphate of Baryta.—Paul Rohland.—Sulphate of baryta, on account of its insolubility, behaves in a manner different to the other sulphates already examined by the author (*Zeit. Anorg. Chem.*, vol. xxxv., p. 210; *Bull.*, 1903, vol. xxxii., p. 645). In any case, according to the researches of Fraps, we know that the former remains in solution in the presence of AlCl_3 , FeCl_3 , and MgCl_2 . The solubility is greatest with AlCl_3 and least with MgCl_2 . This augmentation of solubility appears to be analogous to that observed with sulphate of lime in the presence of NaCl , SO_4Na_2 , CaCl_2 , MgCl_2 , and AmCl_3 —a solubility which reaches a maximum below 37.5° (solubility=ratio between SO_4Ca and NaCl . . .). We observe with SO_4Ba a process of hardening analogous to that of kaolin, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. By shaking up heavy spar powdered as finely as possible with a 10 per cent solution of the salts mentioned above, we obtain a plastic mass containing 12 to 13 per cent of water and 1.1 to 1.4 of salt. Heated to about 580° the mass loses 11.64 per cent of its weight. The author has succeeded in obtaining a substance having a hardness of 2.5, intermediate between that of gypsum (2) and natural heavy spar (3). It is necessary to look for the cause of the phenomena in the two following reactions:—



With salts of iron and magnesium, only the second reaction intervenes.—*Zeit. Anorg. Chem.*, vol. xxxviii., p. 311.

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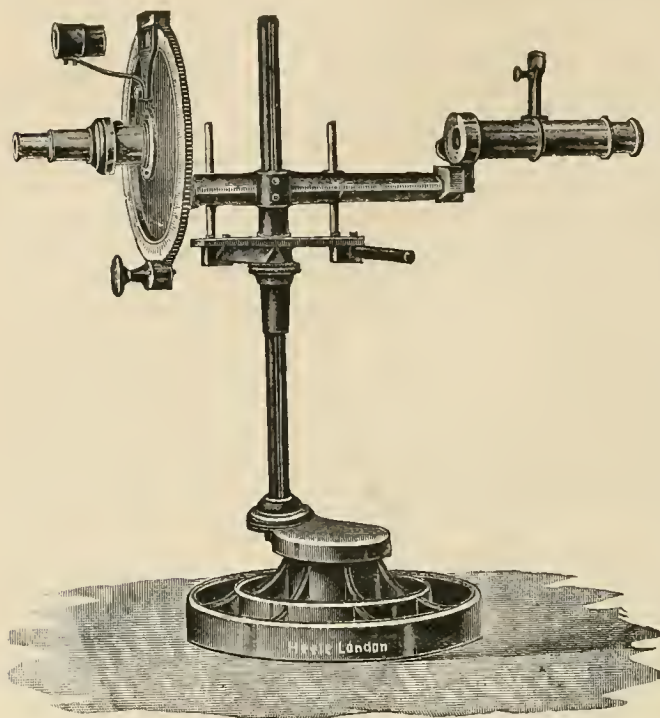
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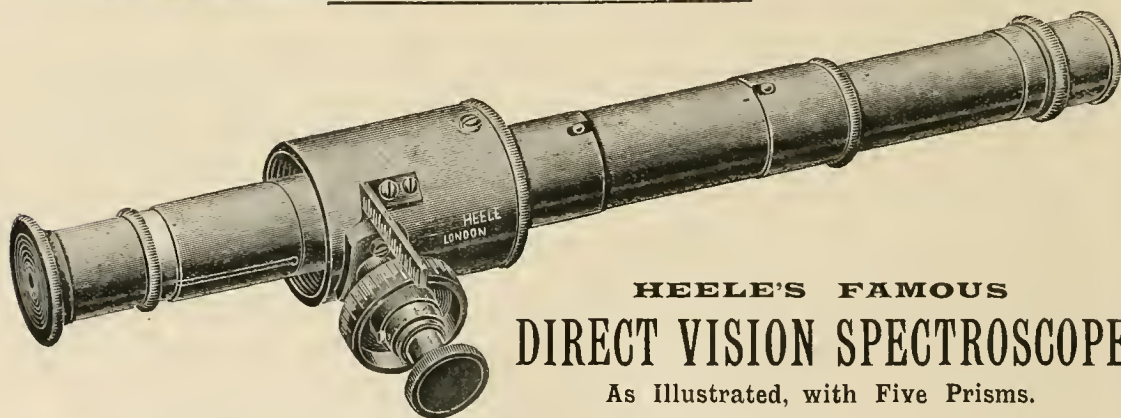
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THORIA, THE ESTIMATION AND SEPARATION OF FROM THE YTTRIUM-CERIUM GROUP OF OXIDES.

By W. B. GILES, F.I.C.

ON reviewing the various methods of separation that have been proposed by different chemists for the separation of thorium from the other members of this group of earth metals it will be found that all of them in practice leave something to be desired. In some of these methods the separations are imperfect, and have to be repeated many times. To this class belongs the method depending upon the solubility of thorium oxalate in ammonium oxalate, with subsequent precipitations with sodium thiosulphate. Take, for instance, the method published by Fresenius and Hintz for ascertaining the purity of commercial thorium nitrate (Truchot, "Les Terres Rares," pp. 304—305). They direct 20 grms. of the nitrate to be dissolved in 3 litres of water; this solution is then to be precipitated by sodium thiosulphate, the precipitate re-dissolved in hydrochloric acid, and this operation repeated five times over. It also involves two fusions with potassium bisulphate, eight resolutions in hydrochloric acid, two resolutions in nitric acid, five precipitations with ammonia, two with sodium hypochlorite, and one with oxalic acid, yielding finally 0.0186 of ceric oxide (impure)! Other methods employ reagents difficult to prepare, such as potassium nitride (Dennis), and in another class, organic substances, such as aniline (Kolb); fumaric acid and metanitrobenzoic acid (Metzner) have been proposed. The introduction of organic matters with a high percentage of carbon and the use of alcohol is undesirable if it can be avoided. In making analyses of minerals containing the rare earths, the author experienced difficulties in accurately separating thorium from the other allied bodies, and he sought for a method of effecting this which should embrace the following advantages. It should be simple and at the same time effective, *i.e.*, it should not require more than one or at most two repetitions for an absolute separation. Finally, it should introduce nothing into the solution which cannot be easily removed, thus facilitating the after estimation of the other constituents. After a course of experiments with a large number of reagents he found that in pure lead carbonate we have a very valuable reagent for the estimation and separation of thorium and some other bodies (zirconia, ceric oxide, and ferric oxide) from the cerium-yttrium group of earths. If we take a solution of these bodies in the form of nitrates, either neutral or slightly acidified with nitric acid, and stir in an excess of pure moist precipitated carbonate of lead, the following results are obtained:—

Wholly Precipitated—

Thoria.
Zirconia.
Ceric oxide.
(Ferric oxide).

Slowly and Imperfectly Precipitated—

Uranic oxide.
Chromium sesquioxide.
(Alumina).

Not Precipitated—

Cerous oxide.
Lanthana.
Neodymia.
Praseodymia.
Yttria.
Samaria.

And the yttria group generally as far as has been noticed.*

In carrying out these experiments, if correct results are desired, it is absolutely essential to have the carbonate of lead *pure*, as in the course of the author's preliminary experiments he met with some anomalous results which were ultimately traced to impurities in the (so-called C. P.) lead carbonate employed). These impurities consist of alkaline carbonates, basic acetates, and nitrates, and almost invariably some ferric oxide. Lead carbonate retains traces of fixed alkaline carbonates with great tenacity (as is the case with calcium, barium, and strontium carbonates), and these cannot be removed entirely with any reasonable amount of washing. Therefore, even at the risk of appearing somewhat tedious, it is well to describe how a pure and suitable lead carbonate is obtained.

"Re-crystallised pure lead nitrate" is dissolved in about five times its own weight of water, warmed to about 70° C., and then sufficient solution of re-sublimed ammonium sesquicarbonate is added to cause a decided precipitation; the whole is kept well agitated, and from time to time a little of the turbid fluid is withdrawn, filtered, well acidified with pure nitric acid, and ammonium thiocyanate added; if any signs of colouration ensue the agitation is continued until every trace of iron has disappeared. The cold solution is then filtered through a close filter-paper, and the clear bright solution is poured in a thin stream with constant stirring into an excess of a clear saturated cold solution of re-sublimed ammonium sesquicarbonate. Reversing the operation by pouring the ammonium carbonate into the lead nitrate leads to the formation of

* Further experiments are in progress with some of the least basic constituents of the yttrium group of metals.

basic lead nitrates and does not answer. The precipitated lead carbonate is allowed to subside and then washed, best by decantation with distilled water, and finally is collected on a filter of toughened paper, and further washed till about half a litre of the washings, to which a drop or two of methyl-orange solution is added, shows a decided acid reaction with two drops of normal nitric acid. It requires a considerable amount of water to remove the last traces of the ammonium carbonate, which of course is indispensable. The lead carbonate is then allowed to drain and dry in a warm place till it becomes pasty, and in this state it is removed into a wide-mouthed stoppered bottle and preserved for use. It acts much better in this moist state than when it is dried, and is more easily diffused in the solutions of the nitrates.

The following experiments selected from a great many examples are given to show the completeness of the separation effected with carbonate of lead. The purest thorium nitrate obtainable, labelled "Thorium" Nitrate Absol. Chem. Pur.," was taken. A solution of this was prepared so that 100.0 c.c. equalled 1 gm. of the crystallised nitrate.

100.0 c.c. precipitated with a slight excess of ammonia, the precipitate washed, dried, and ignited by blast-lamp, gave thoria 0.4785 gm. 100.0 c.c. of the same solution was treated with excess of the moist carbonate of lead, and frequently stirred for twelve hours; then the insoluble matter was collected on a filter, washed, and the filtrate kept. The precipitate was dissolved in the smallest possible amount of dilute nitric acid suitably diluted, and the lead removed by passing sulphuretted hydrogen. The lead sulphide being filtered off, the filtrate was boiled, evaporated somewhat, and precipitated by ammonia; the precipitate washed, dried, and ignited over the blast-lamp. The ignited precipitate weighed 0.4765 gm. The filtrate from the carbonate of lead treatment was treated with sulphuretted hydrogen in the same way; after filtering off the lead precipitate the solution was boiled to a small bulk and heated with ammonia and a little ammonium oxalate. A small precipitate was obtained which, when collected, washed, dried, and ignited, weighed 0.0015 gm.; it was of a chamois colour, and on being dissolved in hot strong sulphuric acid it gave the reactions of cerium with ammonium persulphate, and also with hydrogen peroxide in the solution rendered alkaline by ammonia. So that this trial separated at one treatment 0.15 part of ceria-yttria oxides from 47.65 parts of thoria contained in the so-called "Thorium Nitrat. Absol. Chem. Pur." This may be contrasted with the marvellously complex process of Fresenius and Hintz by which they separated ultimately 0.1357 part of ceria, neodymia, lanthana, and yttria from 46.2666 parts of thoria. Still even this mode of procedure leaves something to be desired, as the ignited thoria precipitate was not perfectly white, and it was found that this occurred because a small portion of the cerium in the thorium nitrate existed as ceric nitrate. Solutions of cerous nitrate are readily oxidised when evaporated with nitric acid. In a trial made with a solution of cerous nitrate evaporated twice to dryness on the water-bath with nitric acid of 1.520 specific gravity, nearly 50 per cent of the total amount of cerium was converted into the ceric form, and as ceric nitrate is completely precipitated by lead carbonate, the necessity of being absolutely certain that all the cerium exists in the cerous form is evident. The best method of attaining this is to heat the dilute solution with hydric sulphide, and then to boil off the excess without allowing the solution to become concentrated or highly acid.

Sulphurous acid may also be employed to reduce any ceric salt. Therefore, to separate the traces of foreign earths in commercial thorium nitrate, dissolve in water about 1 to 2 grms. per 100 c.c., pass a current of H_2S , boil off the gas completely, and keep up the amount of water

evaporated. When cold, add moist carbonate of lead, and proceed as described.

After dissolving the washed precipitate of thoria with excess of lead carbonate and separating the lead as sulphide, it is evident that it is easy to repeat the separation by adding a fresh portion of carbonate of lead. However, the amount of any foreign oxides thus separated is so minute that it is generally hardly worth the additional trouble that it entails. In these first experiments a great excess of thoria was associated with a minute amount of foreign oxides; in those to be described the amounts of ceria-yttria oxides were in some cases equal to the amount of thoria, and in some instances only traces of thoria were dealt with, mixed with a very large amount of the other earths. It was at first contemplated that the cerium-yttrium group of earths should be treated one by one to ascertain how they behave with lead carbonate when they were associated with thoria.

But it was found that this would entail a vast amount of work, and further that many of these oxides were scarcely obtainable in a state of purity, and so it was resolved to deal with them collectively, as by this means one would realise the actual conditions generally encountered in the analysis of minerals containing the rare earths. The technical working up of large quantities of monazite sands for the preparation of thoria yields as by-products, for which little use has yet been found, very considerable quantities of the salts of the cerium-yttrium group of metals, and among these a product is found in commerce under the name of "Crude Cerium Nitrate." It forms a dry nearly white granular powder with a faint rosy hue, and smelling slightly of nitric acid. A quantity of this was obtained and examined, in the first place, qualitatively. It was found to contain only faint traces of iron, calcium, or magnesium, no phosphate, chloride, or sulphate, a little free nitric acid, a small amount of thoria (0.67 per cent), about 19.4 per cent of ceric oxide, and about 19.57 of other rare earthy oxides, comprising lanthana, neo- and praseodymia, samaria, and also metals of the yttria group. It dissolved in water readily, giving a slightly opalescent solution, and when this solution was precipitated with oxalic acid it yielded oxalates of a faint rose colour, which on ignition gave oxides of a bright brown colour which amounted to 39.64 per cent on the nitrates employed. These nitrates were treated as follows:—40 grms. were dissolved in about a litre and a-half of distilled water, filtered, and the clear filtrate treated with excess of hydric sulphide. There was no sign of any heavy metals, even on standing. The sulphuretted hydrogen was then boiled off, and when cold an excess of pure moist carbonate of lead was added, and the whole kept well stirred for twenty-four hours. The precipitate was filtered off, well washed, and dissolved in the smallest possible amount of nitric acid, diluted, and the lead precipitated as sulphide; this was filtered off, washed, and the solution was concentrated to about 50.0 c.c. To this solution, when boiling, was added a hot solution of pure oxalic acid in slight excess, the whole allowed to stand twelve hours, and the oxalate washed with hot water and dried at 100° C. The oxalate was then removed from the filter-paper as far as possible into a small porcelain crucible, further dried to a constant weight at 100° C., and then weighed. 0.369 gm. of oxalate gave 0.2175 gm. of a white oxide equal to 58.94 per cent, which agrees almost exactly with the composition of thorium oxalate dried at 100° C. The oxide dissolved in sulphuric acid diluted with an equal amount of water after considerable digestion, and this solution at a suitable concentration yielded a fluid which when heated became semi-solid from the separation of the characteristic "cotton-wool sulphate," which dissolved again on cooling. When the few drops of mother-liquor which could be separated from this hot pasty mass were drained off, dissolved in water, and excess of ammonia and hydrogen peroxide added, there was a slight but distinct evidence of ceric peroxide. But when hydrogen peroxide was added to the slightly acid and rather concentrated solution, a heavy

* This sample of thorium nitrate was obtained some time ago, before the practice of adding intentionally 1 per cent of ceria was in vogue.

precipitate of thorium peroxide sulphate formed at once. So that it is clear that the great mass of the precipitate was thoria, as the composition of the oxalate shows, but that it still contained slight traces of ceric oxide, which would be entirely removed by a repetition of the treatment with carbonate of lead. However, the present object was only to obtain a solution of earth nitrates quite free from thoria. The quantity of thoria obtained from the nitrates in this manner amounted to 0.602 per cent on the original nitrates, showing that the commercial extraction of the thoria had failed to remove this amount.

(To be continued).

ON TERBIUM AND SOME OF ITS COMPOUNDS.

By EMMA A. POTRATZ.

THE metal which is the subject of this paper was discovered and described in 1843, under the name of erbium, by Mosander, confirmed by Berzelius, Scherer, and others. Later on Bunsen and several other chemists denied the discovery of Mosander and applied the name *erbium* to another metal also discovered by him. Delafontaine and Marignac demonstrated simultaneously the individuality of the Swedish chemist's erbium; but in order to avoid confusion, they proposed that the name *terbium* be transferred to the erbium of Mosander, which was accepted. Since 1880 terbium has not been the object of extended researches, not to my knowledge at least. As will be seen, the results here described confirm and extend those of the two chemists of Geneva and Chicago.

Terbium belongs to that large family known as the rare metals, rare earths, cerite and gadolinite metals, &c., having three characteristics in common:—that their oxides, powerful, salifiable bases, cannot be reduced by ordinary means, and form salts possessing a more or less sugary and astringent taste. It acts like the rare earths with oxalic acid, the alkaline oxalates, potash, potassium sulphate, in addition to which it has characteristics of its own, which leave no doubt about its individuality as an element, such as the lack of colour of its solutions, its specific gravity, molecular weight, spectrum, &c.

The salts of the members of the didymium and erbium groups are coloured and show characteristic absorption spectra, which is not true of the terbia compounds.

Lanthanum and yttrium differ by their beautiful spectrum of brilliant lines, their atomic weight, the whiteness of their oxides, &c.

The solutions and solid salts of samarium are yellow and give a specific absorption spectrum.

Terbium and decipium (the so-called gadolinium of some chemists) have different atomic weights and spectra.

Terbium oxide, Tb_2O_3 , is a brownish-orange powder like some varieties of ochre. Its specific gravity is 6.27. The shade of the colour varies from a lighter to a darker tint according to whether the oxide was prepared from the formate, the acetate, or the carbonate, &c. It is a very powerful base, equal in that respect to didymium oxide. It really combines with moderately dilute acids, with a very slight evolution of gas, even after it has been recently and strongly ignited. That is due to a very incomplete sur-oxidation. A very small quantity of water is formed when terbia is heated in a current of H. After that treatment terbium oxide is white and opaque. The oxide, after that calcination, dissolves readily in acids. A moderate calcination in an open dish restores the original colour of the reduced terbia, unless it has been ignited at a very high temperature. An unsuccessful attempt was made to prepare a higher degree of oxidation of terbium.

A very cold solution of terbium sulphate was mixed with hydrogen peroxide and precipitated by pure ammonia. The precipitation was attended by a slight evolution of O. The gelatinous hydrate assumed a very pale greenish colour by drying at the ordinary temperature. The

analysis of that product showed it to be a mixture of terbium hydrate and a very small proportion of a higher oxide not in definite proportions. Moreover, in spite of a careful washing it retained some basic sulphate, for when dissolved in dilute HCl, after reduction in H, it emitted a gas with a strong odour of H_2S . Terbium hydrate, $Tb_2O_3 \cdot 3H_2O$, is like cerous hydrate in the air. It obstinately retains a small quantity of acid, even when the precipitation has taken place in the presence of a strong excess of ammonia. It draws the carbonic acid of the air; combines easily with the acids. It contracts very much by drying and becomes quite opaque. It contains 13.23 per cent of H_2O , which is expelled by a strong heat and leaves Tb_2O_3 in dark brownish-orange lumps.

Terbium has such a tendency to make basic salts that it is not advisable to try and make its hydrate by throwing it down by ammonia. A better way is to pour the terbium solution into an excess of caustic potassa, &c.

Colloidal Compounds.

Like yttrium acetate, the corresponding terbium salt is capable of producing a colloidal compound which is evidently a soluble hydrate, although it always retains a very small proportion of acetic acid, as Delafontaine has shown to be also the case with colloidal yttrium hydrate. Ultimately the solution of the colloidal terbium hydrate coagulates and settles at the bottom of the bottle. After a strong calcination it leaves Tb_2O_3 with its natural intense colour.

Terbium Chloride.

This compound is easily obtained by dissolving terbia in moderately dilute HCl and evaporating the clear colourless solution. Owing to its very great solubility it crystallises with difficulty. The tabular crystals are deeply truncated, rectangular octahedra.

By the application of heat it loses its water and melts into a pasty mass, which seldom re-dissolves completely in water owing to the formation of a more or less copious residue of oxychloride. That is why no attempt has been made to obtain free Tb by decomposition with K or Na. The electric furnace which has given such remarkable results in the hands of Moissan, would probably give a purer product.

Terbium Bromate, $Tb_2O_3 \cdot 3Br_2O_5 \cdot 18H_2O$.

This was obtained by neutralising bromic acid with terbia. It crystallises spontaneously and forms colourless, transparent glistening crystals, not deliquescent, containing 18 molecules of water. They are hexagonal, deeply truncated pyramids, probably isomorphous with didymium bromate.

Analysis.

		Found.
Tb_2O_3	 25.33	25.60
18 aq.	 23.17	23.00
$3Br_2O_5$	 51.50	

Terbium Perchlorate.

Perchloric acid neutralised by terbia gives a clear colourless solution. After evaporation, the perchlorate is left in very small crystals which soon re-dissolve in the mother-liquor. This solubility is so great that no attempt was made to analyse that salt. The perchlorate is also very soluble in alcohol.

Terbium Carbonate.

A solution of pure crystallised ammonium carbonate was used to precipitate a solution of terbium perchlorate. The precipitate was somewhat gelatinous, white, and settled readily. An excess ammonium carbonate did not re-dissolve it. Upon standing in water it did not assume a crystalline appearance, and did not change colour on exposure to air. It dried exceedingly slowly in the air. The analysis gave—

CO_2	 22.52
Tb_2O_3	 61.76
Aq. (by diff.)	 15.72

which corresponds to the formula of a normal carbonate with six molecules of water. By desiccation at 100°C . that salt loses also some CO_2 . The calculated amount of terbia is nearly 59.6 per cent. I have found 61, 61.75, and 63.21 per cent from samples kept in open air from one to three weeks.

Terbium Acetate, $\text{Tb}_2\text{O}_3 \cdot \text{H}_2\text{O} \cdot 8\text{aq}$.

Terbia readily dissolves in warm moderately dilute acetic acid. The colourless solution yields fine transparent colourless crystals. These crystals are four-sided plates with bevelled edges and sometimes with truncated corners, isomorphous with yttrium and didymium acetate. They contain 8 molecules of water, which they lose at a few degrees above 100°C . 100 parts water dissolve 9 parts of crystals at 60°C .

Analysis.—100 parts of crystals, crushed and pressed in filter-paper, gave 18.17 of water and 43.96 of Tb_2O_3 . The theory requires 17.18 of water and 44.03 of base.

Terbium Formate.

As this salt plays a very important part in the separation of terbium, especial care was taken to obtain it as free as possible from the formates of yttrium, didymium, &c. Its solubility is 1.8 in 100 parts of water, or approximately 54 parts water dissolves 1 of formate, which is the average of two closely agreeing determinations. Delafontaine had found that solubility to be about 1 in 35 parts of water, but later on the spectroscope showed that his product still retained some yttrium formate. It is an amorphous, white salt deposited in compact crusts on the sides of the evaporating dish or a white powder. By ignition, it retains its form without swelling up as yttrium formate does. It is anhydrous.

Terbium Meconate.

This salt, which was obtained by neutralising a warm but not boiling solution of meconic acid with terbium carbonate, is an insoluble whitish compound which contains 83.80 per cent of base. The formula for an anhydrous tribasic meconate requires 84.15 per cent. terbia. The meconate when strongly heated, softens, swells up, and turns black. Finally, in the presence of air, all the carbon is burned, leaving nearly 84 per cent terbia.

Terbium Citrate.

Terbia citrate was obtained by neutralising a concentrated cold solution of citric acid by terbium carbonate. The clear colourless solution of that salt leaves by spontaneous evaporation a varnish-like transparent residue without any appearance of crystallisation. The solubility of the citrate decreases with the temperature. At about 45° the solution becomes cloudy, the cloudiness increases as the thermometer runs higher until 85° or so, where the curdy precipitate becomes pulverulent and the thermometer remains stationary for several minutes. When the liquid is cold again, the citrate re-dissolves without leaving any residue. While drying, the separated citrate forms a transparent coating on the sides of the filter, and the filtrate still retains much dissolved citrate, which is thrown down by means of strong alcohol.

Terbium Carbide.

Calcined in a closed crucible, the organic salts of terbium, especially the formate and the acetate, leave a black, charcoal-like residue which consists of terbium carbide with a small proportion of oxide and free carbon. The product is purer if the decomposition is carried on in a tube through which passes a stream of pure dry H. The residue catches fire and burns like tinder when it is thrown on a table. That product is stable in the air, if it is allowed to cool in an atmosphere of H. Very dilute acids dissolve very little of terbium oxide and leave the carbide TbC_3 between 98 and 95 per cent pure. The carbide thus obtained does not acquire the metallic lustre by rubbing it in an agate mortar. A better way to obtain that and the

similar compounds of the other metals would be by using the electric furnace as M. Moissan does.

Extraction.

The terbia used in my experiments was extracted chiefly from samarskite, in the shape of mixed earthy fluorides decomposed by sulphuric acid, and transformed into oxalates and lastly into nitrates as usual. After the separation of thorium and uranic oxide, the solution of the mixed earths was separated into compounds of the cerium and the yttrium groups. The latter treated thrice with sodium sulphate afforded a further separation into insoluble sodium double sulphates and soluble ones. Terbia was thus concentrated into the former, extracted, re-dissolved in nitric acid, and thrown down in fractions by oxalic acid, as usual. The latter treatment repeated several times gave a strongly coloured base after ignition of the oxalate. That base was then subjected to a number of treatments by formic acid until no yttria was left, as shown by the spectroscope; a small quantity of didymium concentrated in the final product was removed by a last treatment with potassic sulphate, which reduced it to less than one part in 10,000.

Atomic Weight of Terbium.

Apparently the best method for the determination of the atomic weight of the rare earths is by the synthesis of the sulphate. Wyrouboff was the first, I believe, to show the practical difficulties attending the application of that method to some of the earths; I met the same in the case of terbium.

The complete expulsion of the excess of sulphuric acid takes place at a temperature so near that at which the normal sulphate commences to decompose, that the exact moment at which to stop the heating of the salt is hard to ascertain. Therefore I have confined myself to the analysis of the dehydrated sulphate by precipitation with ammonium oxalate. One sample made from an earth spectroscopically free from Y, Dp, Yb, and Sm gave $\text{Tb}_2\text{O}_3 = 355.8$; Tb = 153.9.

Water	19.20
Tb_2O_3	48.24
SO_3 (diff.)	32.56

100.00

Another sample gave Tb = 154.2. A sample of well purified formate gave 61.60 per cent of base (Tb = 154).

Carefully dehydrated crystals of acetate left 53.65 per cent of base (Tb = 153.1).

No serious error will be made by adopting 154.

The description of the sulphates, double sulphates, and nitrates will be given in another paper with a more extended report on the atomic weight of terbium.

Chicago (U.S.A.), June 3, 1905.

NOTE ON THE ESTIMATION OF FAT IN MILK BY THE LEFFMANN-BEAM PROCESS.

By L. DE KONINGH.

In using this method it is sometimes impossible to get an accurate reading, owing to the formation of a fluffy substance between the fatty and acid layers. This fluffy matter may, however, be readily removed and broken up by means of a very thin metallic wire.

"Glucinum" v. "Beryllium."—M. Delafontaine draws our attention to the fact that Fourcroy settled this controversy in favour of "glucinum" when he said, in the second volume of his "Système des Connaissances Chimique," that it was crystallography which prompted Haüy to request Vauquelin to re-analyse emerald and beryl, resulting in the discovery of a new earth for which Vauquelin, Guyton, Chaptal, and Fourcroy adopted the name Glucine. Previous to Vauquelin's work, Bindheim and Klaproth had mistaken glucina for alumina.

ON THE SPECTRA OF TERBIUM AND OTHER METALS OF THE RARE EARTHS.

By M. DELAFONTAINE.

IN spite of the efforts of many chemists, our knowledge of the rare metals is still in a state of great confusion. The spectroscope, so useful in other lines, has led to widely different conclusions; not that the instrument itself is unreliable, but because it was applied to the study of evidently impure materials, and not always used under the proper conditions.

If there is one element whose identity is well established in the minds of many, that is yttrium. As long ago as 1878, however, I pointed out various facts showing the existence of at least another metal in it. But because the spectroscope seemed to go against my conclusions they were not accepted. That was natural enough: M. Thalén's famous work was supposed to have been done with material of the greatest purity; Bunsen's work was done with an instrument of low dispersive power (it did not separate the sodium lines) and his yttria was manifestly impure, as was proved later.

Thalén first mapped out 86 yttrium lines, but reduced them later to 43. (He has also reduced the number of his lines above 600 units from 19 to 11). Then came Rowland's splendid revisions, in which he gives 42 wave-lengths in the region covered by Thalén (from 4084 to 64352). But there are in the Upsala physicist's table 23 lines not in Rowland's, and 18 in Rowland's not in Thalén's. In that comparison I call identical those lines not more than 1·0 unit apart (such as 4422·00 and 4422·8, or 4374·0 and 4375·1).

The causes of error are such that an absolute agreement is not to be expected in every case. However, the skill of each of them justifies the smallness of the differences adopted by me. Thus, spectroscopically, there is an old and a new yttrium.

My own investigations were carried on during the last eight or nine years with a one-prism spectroscope of a comparatively low dispersive power, but mostly with a spectrometer with a Rowland's opaque flat grating of 14,438 lines to the inch (about 26,000 lines altogether).

The graduated circle allows readings up to 10'', D₁ and D₂ are shown about 2' apart to the 2nd order spectrum. The observed spectra were from different chlorides extracted from gadolinite, samarskite, and fergusonite, freed as much as possible from terbia and the earths of the cerium group. My own readings were all verified by Miss Potratz. To obtain good results, the condensed spark must be as strong as possible and the chloride solution near the point of saturation. But, nevertheless, some regions present a great variability under conditions apparently identical.

A number of times have I obtained spectra almost identical with Thalén's, and when I compare my results with those of Rowland's I am forced to the conclusion that Thalén's last yttrium was a mixture of at least two metals. I separated long ago a metal which I called Philippium, the not completely pure chloride of which gives about 50 lines not in Rowland's yttrium spectrum; the majority of them are seen in the old Thalén's yttrium. Of the lines of my philippium five belong perhaps to terbium, three to yttrium, and three doubtfully to scandium.

Under the best conditions the spark spectrum of terbium appears as a narrow continuous spectrum, faint at the red end but growing more intense towards the violet. That luminous coloured band is crossed by a great many bright lines; two, quite fugacious, are in the yellowish end of the orange, very few in the yellow and yellowish green; they increase in numbers and brilliancy from the green to the violet, where they are so close together and variable in intensity that it is possible to measure only the most conspicuous ones (in the green and blue).

The following is a list of some of the appropriate wave-lengths observed in the region between 600 and 430:—

597·957		506·236
582·604		505·594
566·2		505·4
550·623		502·93
539·177		498·87
529·470		488·05
525·038		481·5
524·5		466·42
520·066	Double	464·2
518·928	Faint	464
518·00		460·118
514·820	Strong	450·56
512·10		434·32
510·48		431·63
516·16		438·28
507·0		432·5

None of the above lines occurs in the yttrium (Rowland's), samarium, decipium (gadolinium) spectra.

The reversal of spectral lines has been observed in numerous instances. Generally the reversed lines are the brightest of the spectrum. Barium, bismuth, cadmium, copper, iron, &c., afford good illustrations of that phenomenon.

I have once observed the reversal of the Di and Sm spectra under conditions different from those described by Bunsen. A solution of terbium chloride containing a very small proportion of Di and Sm (less than 1 per cent) was being sparked in front of a one-prism spectroscope. The spectrum appeared as a narrow band of light, almost continuous but faint, crossed by numerous lines of variable intensity. When the current lost some of its strength so did the bright lines, but there appeared also about thirteen narrow sharply limited black lines, which occupied the position of so many coloured lines of Di, Tb₃, and Sm₃. Another interesting feature: the liquid below the spark assumed a yellow colour and showed—above the luminous band—the absorption lines of the two metals, but broader, with their usual haziness at the edges. The space above the solution exhibited a fine lavender coloured bloom.

Chicago (U.S.A.), June 3, 1905.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, June 14th, 1905.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

Mr. G. W. T. Horrod was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Harry Dunlop, Cragdarroch Cove, Dumbartonshire; Eric Haydn-Morris, care of Messrs. G. Mowling and Son, Footsray, Melbourne, Victoria.

The PRESIDENT announced that it had been decided by the Council that the ordinary meetings of the Society shall be held during the ensuing Session on the first and third Thursdays at 8.30 p.m.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Edward Williams Bealey, B.A.; William J. Bees, B.Sc.; Joseph Bennett; William Robert Bousfield, M.A., K.C., M.P.; Eric William Campbell; William Beaverly Cowie; William Walpole Day, B.Sc.; Ralph Emerson De Lury, M.A.; Robert Donald, M.A., B.Sc., M.R.C.S., L.R.C.P.; Ernest Lyle Carman Foster, M.A.; Herbert Henstock, B.Sc.; William John Jarrard, B.Sc.; Arthur Walter Mason, B.Sc.; Frederick Wilson Montrose Ross; James Steger, B.Sc.; William Bradshaw Tuck; John William White; William James Wren.

Of the following papers, those marked * were read:—

*121. "Influence of Various Sodium Salts on the Solubility of Sparingly Soluble Acids." By JAMES CHARLES PHILIP.

That magnesium hydroxide is more soluble in ammonium chloride solutions than in pure water is due, according to one current explanation, to the formation of undissociated ammonium hydroxide, and the consequent removal of hydroxyl ions, this leading to the solution of more hydroxide. If this is so, then conversely the solubility of sparingly soluble acids should be increased in the presence of sodium salts of weak acids. This is found to be actually the case, and the influence of sodium formate, acetate, and butyrate, on the solubility of cinnamic, benzoic, salicylic, and *o*-nitrobenzoic acids has been determined at 26.4°. It is to be expected on theoretical grounds, and the expectation is confirmed by the experimental results, that the extent to which the solubility of a given sparingly soluble acid is increased by the presence of the sodium salt NaA will depend on the strength of the acid HA. If the concentration of the sparingly soluble acid in the saturated solution is plotted against the concentration of the added salt (NaA, NaA', NaA'', &c.), it is found that the order of the curves so obtained is the order of strength of the acids HA, HA', HA'', &c. Further, the increase of solubility of cinnamic acid, for example, in solution of NaA of known concentration, as compared with its solubility in pure water, can be calculated in good agreement with experiment when the solubility product for cinnamic acid and the dissociation constant of the acid HA are known.

*122. "The Dielectric Constants of Phenols and their Ethers Dissolved in Benzene and *m*-Xylene." By JAMES CHARLES PHILIP and DOROTHY HAYNES.

Evidence was brought forward some time ago by one of the authors (Philip, *Zeit. Physikal. Chem.*, 1897, xxiv., 18) showing that the dielectric constant of an alcohol calculated from the dielectric constant of its benzene solution decreases as the concentration of the alcohol decreases, and is in all cases less than the directly determined dielectric constant of the pure alcohol. This behaviour, connected probably with the associative tendency of the alcohol molecules, has now been observed also in the case of phenols. The phenomenon is well marked in the case of phenol itself, but less distinct in the case of the cresols; indeed, the dielectric power of *o*-cresol in benzene solution seems to be nearly independent of the concentration. The phenol ethers, in which the associative tendency has been got rid of by obliterating the hydroxy-group, exhibit an almost dielectric behaviour in benzene solution. It is noteworthy that the introduction of a methyl group at any point in the ring lowers the dielectric constant of anisole, the lowering effect, however, of the methyl group being much greater in the ortho-position than in either the meta- or para-position.

DISCUSSION.

Sir WILLIAM RAMSAY inquired whether Dr. Philip's measurements threw any light on the fact that the molecular weight of alcohol in benzene solutions may rise as high as 230. Was this due to polymerisation of the alcohol or to a compound of alcohol with benzene?

Dr. PHILIP said that although the dielectric property of alcohol in benzene had been found to diminish with dilution in an analogous manner to the molecular weight, no evidence had been obtained bearing on the point referred to by Sir William Ramsay.

*123. "Synthesis by Means of the Silent Electric Discharge." By JOHN NORMAN COLLIE.

When pure ethylene was submitted to the action of the silent electric discharge in a vessel cooled to -20°, polymerisation occurred, and a liquid was produced together with some hydrogen gas. In one experiment, 210 c.c. of ethylene gave about 40 c.c. of hydrogen.

Ten grms. of the liquid produced by the polymerisation of ethylene were fractionated. The fractions collected, and their analyses were as follows:—

	100°.	100—150°.	150—200°.	200—250°	Residue.	Distilled residue.
C ..	83.4	85.3	85.8	86.0	87.7	87.7
H ..	16.0	15.3	14.3	14.0	12.4	12.3

The first fraction was very small; most of the distillate collected in the two fractions 100—150° and 150—200°, the chief part boiling between 130° and 170°. The residue left in the flask was a dark resinous substance, which, on heating, smelt of burnt indiarubber; this product weighed 4 grms., or two-fifths of the whole.

The decrease in hydrogen and increase in carbon in the above analyses is interesting; olefinic hydrocarbons, C₄H₂₄, require C=85.7, H=14.3; C₂₀H₃₄ requires C=87.7, H=12.3 per cent.

These various fractions were oxidised by means of potassium permanganate solution in the cold. After filtering off the precipitated manganese oxide, the solution of potassium salts was acidified; a strong odour of either valeric or caproic aldehyde was at once produced in the case of the two fractions (100—150° and 150—200°). These aldehydes were distilled in steam, and oxidised with silver oxide. The silver salt gave, on analysis, Ag=48 per cent, which is equivalent to an acid of molecular weight 118, that of caproic acid being 116.

Ethylene was also mixed with carbon monoxide, and submitted to the silent electric discharge, when aldehydes were formed in small quantity. Formaldehyde and acrolein were both probably present, but the chief condensation that occurred was that of the ethylene itself to form hydrocarbons having high boiling-points.

The facts that are of especial interest are that ethylene under the influence of the silent electric discharge at the ordinary temperature will not only unite with carbon monoxide, but will also polymerise, yielding a series of complicated hydrocarbons; the chief substances formed boil at about 150—160°, and apparently approximate in composition to C₁₀H₂₀; moreover, further condensation means loss of hydrogen and the formation of compounds approximating both in properties and composition to the terpene derivatives. On oxidation, the olefinic hydrocarbons break down, yielding compounds containing about six carbon atoms in the molecule.

DISCUSSION.

Mr. HARCOURT referred to experiments on ozone by Sir B. Brodie, in which the oxygen exposed in a Siemens tube to the silent discharge was mixed with a large proportion of carbon dioxide, the idea being that ozone might be protected during its formation by dilution with carbon dioxide, and obtained afterwards in a concentrated form by absorption of the diluent. The results, however, showed that carbon dioxide was decomposed and ozone formed from it; moreover, a brown coating was deposited on the glass, this product being readily soluble in water. This experiment seemed to be an illustration of Dr. Collie's view that the syntheses which plants effect under the influence of sunlight, forming complex products out of carbon dioxide and water, may be to some extent paralleled by the action of the silent discharge.

Prof. TILDEN reminded the author that experiments of the same character and having similar results had already been carried out by Berthelot (*Journ. Chem. Soc.*, 1876, ii., 596).

The PRESIDENT considered that not the least interesting part of Prof. Collie's paper was the fact that he had succeeded in obtaining a sufficient quantity of the synthesised products to enable him to give definite and quantitative information as to their nature. Most of the workers who had studied the synthetical action of the silent electric discharge had hitherto only given qualitative results. With reference to the polymerising action of this discharge, he (the President) mentioned that some years ago, in conjunction with Mr. R. J. Strutt, he had made some experiments having for their object the possible combination of argon with acetylene. No combination was observed, but the polymerising action of the discharge on

the acetylene was very obvious, an accumulation of tarry and resinous products being obtained, but these were not further examined, as practically the whole of the argon originally mixed with the acetylene was recovered at the end of the experiments. With respect to photosynthetic processes, he thought it might be of interest, in view of the modern developments of radio-activity, to call attention once again to the older work of Fay, and of Seekamp, who states that photochemical decompositions are in many cases promoted by the addition of uranium salts to the solutions. This raises the question whether the energy, which must be supposed to be liberated on the "disintegration" hypothesis of the uranium atom, may not play a part in such photochemical processes.

*124. "The Ultra-violet Absorption Spectra of Aromatic Compounds. Part I. Benzene and certain Mono-substituted Derivatives." By EDWARD CHARLES CYRIL BALY and JOHN NORMAN COLLIE.

The ultra-violet absorption spectra of benzene and of some of its mono-substituted derivatives were described. It has been found that benzene presents seven separate absorption bands, and it was shown how the formation of these may be accounted for by attributing each one to a separate and distinct process of dynamic isomerism connected with the linking changes within the benzene molecule. In the case of the mono-substituted derivatives of benzene, it is shown how their absorption spectra may be arranged in types, and it appears that each type corresponds either to complete saturation or to the nature and position of unsaturated atoms in the substituent group. The presence of an unsaturated atom in the α -, β - or γ -position in the side-chain thus produces a particular type of absorption. When the unsaturated atom is present in the δ -position, it is apparently removed too far from the nucleus to exercise any effect, with the result that the same absorption spectrum is obtained as if the side-chain were completely saturated.

*125. "The Ultra-violet Absorption Spectra of Aromatic Compounds. Part II. The Phenols." By EDWARD CHARLES CYRIL BALY and ELINOR KATHARINE EWEANK.

The ultra-violet absorption spectra of anisole and phenetole are found to differ from that of phenol; in the former cases, the single absorption band given by phenol is sub-divided near its head into two bands. The absorption band produced by the dynamic isomerism existing in solutions of acetylacetone and similar tautomeric substances of the aliphatic series occupies very nearly the same position as the band given by phenol. The existence of a similar type of dynamic isomerism in the case of phenol would therefore explain the difference between the spectra of phenol and its ethers. The presence of this kind of tautomerism, that is, a labile hydrogen atom, in phenol is proved by the influence of acid and alkali on the spectrum of this substance. Just as in the case of certain aliphatic tautomeric compounds, the position of the absorption band is shifted towards the red on the addition of sodium hydroxide, whilst the addition of acid tends to restrain the dynamic isomerism. The results obtained with the three dihydroxybenzenes, the three cresols, and p -aminophenol support the view that similar tautomerism exists in these substances.

*126. "Association in Mixed Solvents." By GEORGE BARGER.

The association which many hydroxylated substances exhibit in some solvents (benzene, chloroform) does not occur in others (alcohol, acetic acid), probably because the latter form loose molecular compounds with the solute according to the law of mass action (Abegg, *Zeit. Anorg. Chem.*, 1904, xxxix., 330). In dilute solutions, the concentration of the solvent is large compared with that of the solute, and if the solvent is dissociative its influence predominates. The present investigation deals with cases in which the concentration of the dissociative solvent was reduced by mixing it with an associative one.

The dissolved substances were acids, alcohols, phenols,

and oximes. Dilute solutions of these were made in mixtures of toluene, benzene, chloroform, or carbon tetrachloride with one of the following dissociative solvents:—Pyridine, acetic acid, ethyl acetate, methyl acetate, ethyl formate, ethyl alcohol, methyl alcohol, and acetone. The molecular weight of the solute was determined by the author's microscopic method (*Trans.*, 1904, lxxxvi., 286), this process being particularly suited for work with mixtures.

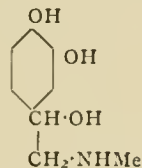
The results are in general agreement with what might be expected from mass action according to the above theory. The molecular weight is normal in nearly all the mixtures, and association only persists when the percentage of the dissociative solvent is very small.

The esters are the least powerful of the dissociative solvents examined, which is in accordance with their behaviour in other respects. For instance, as the result of a study of the boiling-points of homologous series, Young places the esters between associated and non-associated liquids (*Phil. Mag.*, 1905, [6], ix., 1).

According to Lachman (*Journ. Am. Chem. Soc.*, 1903, xxv., 50), brown solutions of iodine owe their colour to the formation of loose molecular compounds between solute and solvent. If equal volumes of an alcoholic and a chloroform solution containing equal quantities of iodine are mixed, the colour of the mixture is not intermediate between that of the component solutions, but is more like that of the alcoholic solution. This experiment serves to illustrate the mass action effect of the solvent.

*127. "Synthesis of Substances Allied to Epinephrine." By GEORGE BARGER and HOOPER ALBERT DICKINSON JOWETT.

The authors have attempted to synthesise a compound having the formula—

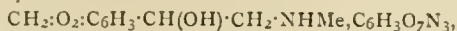


which was proposed by one of them (*Trans.*, 1904, lxxxv., 192) for epinephrine (adrenaline), the active principle of the suprarenal gland.

Although the methylene and dimethyl ethers were prepared, the dihydroxy-base could not be isolated.

The constitution of the ether bases was proved by their oxidation to piperonylic or veratric acid respectively. The dihydroxy-base could not be obtained from the ethers, although indications of the formation of a substance having the chemical and physiological properties of epinephrine were obtained by the action of dilute hydrochloric acid at 150° on the methylene ether.

The following compounds were prepared and described:— α -3 : 4-methylenedioxyphenyl- α - β -dibromoethane, $\text{CH}_2\text{O}_2\text{C}_6\text{H}_3\text{:CHBr}\cdot\text{CH}_2\text{Br}$, needles, m. p. 82–83°; α -3 : 4-methylenedioxyphenyl- β -bromo- α -hydroxyethane, $\text{CH}_2\text{O}_2\text{C}_6\text{H}_3\text{:CH(OH)}\cdot\text{CH}_2\text{Br}$, long needles, m. p. 107–108°; β -3 : 4-methylenedioxyphenyl- β -hydroxyethylmethylamine picrate,—



yellow needles, m. p. 178°; the corresponding base and platinichloride are amorphous; 3 : 4-dimethoxystyrene, $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3\text{:CH}_2\text{:CH}_2$, colourless liquid boiling at 120–125°/10 m.m.; α -3 : 4-dimethoxyphenyl- α - β -dibromoethane, $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3\text{:CHBr}\cdot\text{CH}_2\text{Br}$, needles, m. p. 102°; α -3 : 4-dimethoxyphenyl- β -bromo- α -hydroxyethane, $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3\text{:CH(OH)}\cdot\text{CH}_2\text{Br}$, long needles, m. p. 68°.

The corresponding methylamine base could not be crystallised, nor could any crystalline salt be obtained.

The piperonyldibromide (m. p. 160°) described by Mameli (*Gazzetta*, 1904, [1], xxxiv., 358) is really the dibromohydrin, $\text{CH}_2\text{O}_2\text{C}_6\text{H}_3\text{:CH(OH)}\cdot\text{CH}_2\text{Br}$, and has been obtained by the action of bromine water on the bromo-

hydriin, and also by the action of phosphorus pentachloride on the dibromide.

*128. "The Determination of Melting-points at Low Temperatures." By LEO FRANK GUTTMANN.

A method has been worked out for readily determining melting-points at low temperatures by means of a constantan-copper couple connected to a delicate galvanometer. The couple was calibrated by immersion in substances of known melting-point; ice, chloroform, ether, liquid air, and a mixture of solid carbon dioxide and alcohol being chosen. The melting-point of ethyl bromide had been determined by a previous observer to be -129.5° , and it is now shown to be -118° , the low number formerly obtained being due to an admixture of ether. The melting-point of some very pure toluene was also found to be higher than that of ordinary pure toluene, to which the melting-point -97° to -99° had been ascribed.

The melting-points determined were methyl alcohol, -98° ; ethyl alcohol, -117.3° ; methyl iodide, -64° ; ethyl chloride, -142° ; ethyl bromide, -118° ; ethyl iodide, -109° ; toluene, -92° ; *m*-xylene, -55° ; ethylbenzene, -93° .

Ethyl alcohol was found to have the property of supercooling to a remarkable degree. It could be frozen to a clear transparent glass by immersion in liquid air, and if it was then allowed to warm up slowly to 135° , crystallisation set in explosively, the temperature rising about 20° in ten seconds, and a white opaque mass of crystallised alcohol being formed.

129. "The Action of Water on Diazo-salts." (A Preliminary Note). By JOHN CANNELL CANE and GEORGE MARSHALL NORMAN.

One of the authors has shown (*Trans.*, 1903, lxxxiii., 688) that little or no hydroxy-compound is obtained by boiling certain ortho-substituted diazo-salts of the diphenyl series with dilute acids, but that quinonoid derivatives resulted. As there are a large number of similarly substituted compounds belonging to the benzene series which are said not to yield the corresponding phenols on boiling with water or acids, it appeared to be of interest to examine these with the object, if possible, of elucidating the course of the reaction.

s-Tribromoaniline.—Silberstein (*Journ. Prakt. Chem.*, 1883, xxvii., 98) was unable to obtain any phenolic derivative by boiling *s*-tribromobenzenediazonium sulphate or nitrate with dilute acids, and Orton, in a recent communication (*Proc.*, 1905, xxi., 168), obtained no trace of the phenol either with dilute or strong sulphuric acid. By using the method described in the German Patent 95339, which consists in heating the diazo-solution with a mixture of dilute sulphuric acid and sodium sulphate (applied in the patent to the production of guaiacol from *o*-anisidine), we have been able to isolate the corresponding *s*-tribromophenol (m. p. $92-93^{\circ}$), although the yield is small.

The failure of other observers to obtain this product is no doubt explained by the fact that the decomposition point of this very stable diazo-salt is considerably above 100° , and by using more concentrated sulphuric acid in order to reach a higher temperature a very considerable retarding influence is introduced.

This retarding influence can be measured by determining the "coefficient of decomposition, C," according to the method described by one of the authors (*Trans.*, 1902, lxxxi., 1412). Thus in the case of diazo-benzene chloride, the value of C in the case of the chloride is 0.0298 (*loc. cit.*, p. 1420).

A blank experiment in which an equivalent quantity of sulphuric acid was substituted gave exactly the same number, the diazo-solution containing 0.7 per cent of H_2SO_4 . When, however, the amount of sulphuric acid is increased until the solution contains about 35 per cent of the acid, the value of C becomes 0.0191. It follows, therefore, that an increase in the quantity of sulphuric acid produces an increase in the stability of the diazo-compound (compare *Ber.*, 1890, xxiii., 2994).

s-Trichloroaniline.—Hantzsch (*Ber.*, 1895, xxviii., 685) prepared a solution of the diazo-chloride of this substance, and was unable to detect the formation of the corresponding phenol by the action of heat. He says, "Trichlorodiazo-benzolchlorid lässt sich mit Wasser, ja selbst mit Salpetersalzsäure kochen, ohne Stickstoff zu entwickeln oder sich überhaupt zu verändern."

The authors have found that under the usual conditions of boiling a brown substance is formed, but only by adopting the same method as in the foregoing instances can a small yield of *s*-trichlorophenol (m. p. 68°) be obtained.

o-Anisidine.—Several workers have been unsuccessful in obtaining guaiacol from the diazo-compound of *o*-anisidine. Thus Limpach (*Ber.*, 1891, xxiv., 4136) passed a current of steam through the solution, but could detect no guaiacol (compare also Gattermann, *Ber.*, 1899, xxxii., 1136).

By passing steam through a strongly acidified solution of the diazo-sulphate for several hours, the authors obtained guaiacol, a still better yield being afforded by the foregoing method. In addition to this product, a small yield of a second substance was isolated; this product crystallised in flat square tables (m. p. 89° ; b. p. $310-312^{\circ}$), giving analytical numbers corresponding with those for the mono-methyl ether of *o*-dihydroxydiphenyl $OH \cdot C_6H_4 \cdot C_6H_4 \cdot OCH_3$.

3-Bromo-*p*-toluidine.—Wroblewski (*Ber.*, 1874, vii., 1061; *Annalen*, 1873, clxviii., 147) describes several halogen derivatives of aniline and toluidine, the diazo-compounds of which do not yield halogenated phenols, but give rise to the corresponding substituted hydrocarbons. In a later paper (*Ber.*, 1884, xvii., 2704), he attributes this abnormality to the presence of a small quantity of alcohol in the diazo-derivative. As regards the above compound, this is probably a correct explanation, as a good yield of the bromo-cresol (b. p. 214° ; *Ber.*, 1884, xvii., 2530) is readily obtained by passing steam through an acid solution of the sulphate.

3-Chloro-*p*-toluidine, the diazo-compound of which is said by Wroblewski (*loc. cit.*) to yield no corresponding phenol when treated in a similar way, gave rise to 3-chloro-*p*-cresol (m. p. 191°).

130. "A Precise Method of Estimating the Organic Nitrogen in Potable Waters." By JAMES CAMPBELL BROWN.

Details were given of a process for the estimation of the whole of the nitrogen of organic matter in potable water and sewage effluents.

The process is found to be as accurate for this purpose as Kjeldahl's method is for larger quantities of nitrogenous matter, and it has many advantages over Kjeldahl's process in convenience and speed, and in the absence of the liability to breakage and loss by bumping in glass vessels.

The process essentially consists in the distillation to dryness and subsequent ignition of a mixture of a portion, ordinarily 200 c.c. of the sample, without previous evaporation, with potassium hydroxide and potassium permanganate. The operation is carried on either in a Jena glass or in a copper retort, and the ammonia evolved is estimated by Nessler's solution.

The total carbon of the organic matter was also estimated as carbon dioxide in the residue remaining in the retort, but the results were not so accurate as in the case of the nitrogen, owing to the large amount of carbon dioxide found by blank experiments, which has to be deducted.

The results obtained by this process on a variety of waters are compared with the corresponding values determined by the Frankland, Wanklyn, and Forchhammer methods.

131. "Synthesis of 1:1-Dimethyl- Δ^3 -tetrahydrobenzene." By ARTHUR WILLIAM CROSSLEY and NORA RENOUF.

When 3-bromo-1:1-dimethylhexahydrobenzene (compare *Proc.*, 1905, xx., 242) is heated with alcoholic potash, it loses the elements of hydrogen bromide with formation of 1:1-dimethyl- Δ^3 -tetrahydrobenzene, which is a colourless,

refractive liquid boiling at $117-117.5^{\circ}/770$ m.m., and having an odour of turpentine. It combines with bromine to form 3:4-dibromo-1:1-dimethylhexahydrobenzene, and on oxidation with potassium permanganate yields 3:3-dimethyladipic acid, a fact which definitely proves its constitution.

A mixture of concentrated nitric and sulphuric acids acts on the hydrocarbon very violently, and does not give rise to an appreciable quantity of a nitro-derivative.

The properties of the hydrocarbon are being compared with those of laurole and isolaurole obtained from derivatives of camphoric acid.

132. "Bromine in Solutions of Potassium Bromide." By FREDERICK P. WORLEY.

The solubility of bromine in aqueous solutions of potassium bromide has been determined over a wide range of concentrations at 18.5° and 26.5° . The curves obtained for concentrations below 0.1 gm.-molecule per litre correspond with an additional absorption of two atoms of bromine for every molecule of potassium bromide in solution, probably due to the formation of KBr_3 . The curves for higher concentrations of potassium bromide deviate slightly on the side of increased solubility of bromine, probably indicating the formation of small quantities of compounds higher than KBr_3 .

The application of the principle of mass action does not lead to any knowledge of the constitution of the polybromide formed in the case of solutions saturated with bromine, but with solutions containing varying amounts of bromine insufficient for saturation the results confirm the formation of KBr_3 with smaller quantities of a higher compound.

The variation of the constants obtained, on the assumption that KBr_3 alone is formed may be due to the unequal ionisation of potassium bromide and KBr_3 .

A simple process has been devised for the determination of the quantity of a volatile substance present in a system containing various substances in equilibrium, where estimation by chemical means is not possible. It possesses the great advantage over other similar methods of avoiding the presence of a foreign substance such as carbon disulphide.

133. "Tetramethylammonium Hydroxide." By JAMES WALKER and JOHN JOHNSTON.

A solution of tetramethylammonium hydroxide may easily be prepared by mixing alcoholic solutions of tetramethylammonium chloride and potassium hydroxide. Potassium chloride at once separates, and may be removed by filtration. Tetramethylammonium hydroxide may be isolated from this solution as the pentahydrate, $\text{NMe}_4 \cdot \text{OH} \cdot 5\text{H}_2\text{O}$, by addition of water and concentration in a vacuum. A trihydrate and a monohydrate are also described. Attempts to prepare the anhydrous hydroxide failed owing to decomposition of the monohydrate into trimethylamine, methyl alcohol, and water.

134. "Tetretethylsuccinic Acid." By JAMES WALKER and ANNIE PURCELL WALKER.

Crum Brown and Walker isolated from the product of electrolysis of sodium ethyl diethylmalonate a crystalline substance having the composition, $\text{C}_{12}\text{H}_{20}\text{O}_3$. This substance is now shown to be the anhydride of tetretethylsuccinic acid. It is attacked by alkalis only with great difficulty, but forms sodium methyl tetretethylsuccinate by direct addition with sodium methoxide. This ester salt may be saponified by boiling with aqueous alkalis, and from the salt obtained tetretethylsuccinic acid may be isolated. It is stable in the solid state, but passes in solution or on fusion into water and the anhydride.

135. "The Ultra-violet Absorption Spectra of Aromatic Compounds. Part III. Disubstituted Derivatives of Benzene." By EDWARD CHARLES CYRIL BALLY and ELINOR KATHARINE EWBANK.

Hartley (*Trans.*, 1885, xlvii., 685), in describing the ultra-violet absorption spectra of the three xylenes, showed that the broad absorption band given by the ortho- and meta-compounds was divided into two in the case of the para-

compound. *p*-Xylene therefore gives two absorption bands, while the ortho- and meta-compounds only show one band. In the present paper, the following substances are dealt with, the absorption spectra of the three isomerides being described in each case:—The chlorotoluenes, the dichlorobenzenes, the tolunitriles, the chloroanilines, and the toluidines, the last two compounds being examined in acid solution. In every case the para-compound shows either more absorption bands than the ortho- and meta-isomerides, or the same number of bands with much greater persistence. It may therefore be concluded that the para-compound is always more symmetrical than its two isomerides; that is to say, the motions of the benzene ring, which give rise to the absorption bands, are less disturbed by the para-substitution than by the ortho- and meta substitutions.

136. "Studies in Chlorination. II. The Action of Chlorine on Boiling Toluene." (Preliminary Notice). By JULIUS BEREND COHEN, HARRY MEDFORTH DAWSON, and PERCY FIELD CROSLAND.

The object of the authors' experiments was to ascertain if electrolytic chlorine, evolved in presence of boiling toluene, entered the side-chain like ordinary chlorine or caused substitution in the nucleus. The results show that, under the conditions of the experiments, electrolytic chlorine enters the nucleus only, and also that the rate of chlorination appears to be more rapid than that of ordinary chlorine evolved from pyrolusite and hydrochloric acid. The current was conducted through the mixture of toluene and hydrochloric acid by means of carbon electrodes, a special series of determinations being made to find whether the electrodes acted as carriers. No difference could be detected in the character of the products when ordinary chlorine was used, whether carbon electrodes were present or not. When ordinary chlorine was used, between 80 and 90 per cent of the product was benzyl chloride, the remainder being a mixture of *o*- and *p*-chlorotoluenes. The experiments are being continued.

137. "Purpurogallin." By ARTHUR GEORGE PERKIN. When purpurogallin is methylated by means of methyl sulphate, it yields, in addition to the trimethyl ether previously described (*Trans.*, 1903, lxxxi., 194), the tetramethyl compound, $\text{C}_{11}\text{H}_4\text{O}(\text{OCH}_3)_4$ (found, $\text{C} = 65.18$, $\text{H} = 5.90$, $\text{CH}_3 = 21.57$; pale yellow prisms, $\text{m. p. } 93-94^{\circ}$). *iso*Purpurogallone, for which the formula, $\text{C}_{11}\text{H}_6\text{O}_5$ was suggested, is more probably $\text{C}_{11}\text{H}_8\text{O}_5$ (found, $\text{C} = 60.08$, $\text{H} = 3.54$); it gives on digestion with sulphuric acid in the presence of acetic acid the anhydride, $\text{C}_{11}\text{H}_6\text{O}_4$ ($\text{C} = 65.36$; $\text{H} = 2.80$; minute, yellow prisms melting above 310°), the acetyl compound of which is identical with that prepared by the action of acetic anhydride on *isopurpurogallone* (*loc. cit.*). *iso*Purpurogallone tetramethyl ether, $\text{C}_{11}\text{H}_4\text{O}(\text{OCH}_3)_4$ (found, $\text{C} = 65.57$, $\text{H} = 5.62$; colourless needles, $\text{m. p. } 211-213^{\circ}$), is prepared by the action of methyl sulphate. The acid obtained from purpurogallin trimethyl ether by means of alcoholic potash at 180° (*loc. cit.*) gives numbers ($\text{C} = 62.87$, $\text{H} = 5.07$) corresponding with the formula $\text{C}_{13}\text{H}_{12}\text{O}_5$, and is probably a derivative of *isopurpurogallone*. From purpurogallin tetramethyl ether, a similar compound can be prepared, and further work in this direction is now in active progress.

138. "The Electrolytic Oxidation of Hydroxybenzoic Acids." By ARTHUR GEORGE PERKIN and FREDERICK MOLLWO PERKIN.

Twenty grms. of gallic acid were dissolved in 100 c.c. of concentrated sulphuric acid, and the solution then diluted with about one-third its volume with water, and electrolysed in the anode compartment of an electrolytic cell, when about 30 per cent of a colouring matter was obtained which had the appearance of, but was not identical with, ellagic acid; it gave an acetyl compound melting at $313-316^{\circ}$.

Protocatechuic acid, when treated in a similar manner, gave catellagic acid, $\text{C}_{14}\text{H}_6\text{O}_6$ (the yield being about 25 per cent), the acetyl compound, $\text{C}_{14}\text{H}_4\text{O}_6(\text{C}_2\text{H}_3\text{O})_2$, melted at $322-324^{\circ}$.

The electrolytic conditions employed were such as are generally used for preparing persulphuric acid, namely, moderately concentrated sulphuric acid and a high anode current density. By the electrolytic method, the catellagic acid obtained is purer than when potassium persulphate and sulphuric acid are employed. The reaction is being further studied, and will be extended to other hydroxybenzoic acids.

CORRESPONDENCE.

RADIUM.

To the Editor of the Chemical News.

SIR,—Some years ago Professor Japp, in an Address to the Chemical Section of the British Association, pointed out that whilst in many cases it had been found possible to synthesise inactive separable mixtures of dextro- and lævo-isomers, as well as the inactive inseparable meso-forms, yet in every case where a separation into the active components had been effected, or when either the dextro- or lævo-compound had been separately obtained, such had been brought about by the direct or indirect action of life. The recent experiments with radium, in relation to spontaneous generation, suggest that it might be worth while to institute experiments with the object of ascertaining whether a racemoid mixture of isomers can be separated into the dextro- and lævo-components with the help of radium.—I am, &c.,

L. PARRY.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxi., No. 23, June 5, 1905.

Preparation and Properties of Thorium Chloride and Bromide.—H. Moissan and M. Martinsen.—Thorium chloride (ThCl_4) and thorium bromide (ThBr_4) can be easily prepared by the action of chlorine or bromine on thorium metal. These compounds, however, in an anhydrous state, whether as liquid or vapour, rapidly attack glass and porcelain, and this property renders their preparation in a perfectly pure state very difficult. It also causes a determination of their vapour density to be not altogether accurate. On the whole these two compounds possess general properties very similar to other compounds belonging to this group.

Property of Tin-aluminium, Bismuth-aluminium, and Magnesium-aluminium Alloys.—H. Pécheux.—The author investigates the conditions under which tin-aluminium, bismuth-aluminium, and magnesium-aluminium alloys decompose water.

Action of Oxygen on Cæsium-ammonium.—E. Rengade.—The rapid oxidation of cæsium-ammonium when dissolved in an excess of ammonia gives the whitish rose-coloured oxide Cs_2O_2 , the yellow oxide Cs_2O_4 , and an intermediate dark brown oxide, Cs_2O_3 . All these are crystallised in microscopic crystals. If the oxygen is allowed to act a little at a time in such a manner as to retard the decoloration of the ammonium metal, the latter reacts on the binoxide formed, giving the amide and a hydrate of the protoxide.

Pyranic Phenols.—R. Fosse and A. Robyn.—Dinaphthopyryl bromide and dinaphthopyranol can react several times on a single molecule of polyphenol. The authors obtain a dipyril-diphenol with resorcin and a tripyryl-triphenol with pyrogallol. In these phenols one atom of pyranic oxygen corresponds to each hydroxyl, and they are insoluble in aqueous alkalis and soluble in alcoholic alkalis.

New Reagent for the Detection of Aconitine.—E. P. Alvarez.—Already inserted.

Dilatation and Density of some Gases at High Temperatures. Application of this to the Determination of their Molecular Weight.—Adrien Jaquero and F. Louis Perrot.—The authors find the coefficient of expansion between 0° and 1067° of nitrogen, air, oxygen, carbonic oxide, and carbonic acid gas. By applying these numbers they then calculate the density of the gases at 1067° and their molecular weight with regard to oxygen to be—O = 32, N = 28.0155 , CO = 28.009 , CO_2 = 43.992 .

Osmotic Pressure of Colloidal Solutions.—J. Duclaux.—With certain modifications, the author finds that all the laws relating to ordinary solutions apply equally well to colloidal solutions. From a purely qualitative point of view, the existence of an osmotic pressure tending to produce an expansion of the system explains the indefinite stability of such solutions. On the other hand, it is certain that the semi-permeable membranes formed of colloids, particularly the cellular membranes of living organisms, have not the inertia with regard to osmotic changes which is generally attributed to them.

Bulletin de la Société Chimique de Paris.
Series 3, vol. xxxiii., No. 1.

Research on the Decomposition of the Alkaline-earth Carbonates by the Alkaline Chlorides in the presence of Water.—H. Cantoni and G. Goguella.—Already noticed.

Solubility of some Metallic and Earthy Succinates in Water.—H. Cantoni and D. Diotalevi.—A long paper, containing many tables and diagrammatic curves, not suitable for abstraction.

Stimulative and Paralysing Influences of certain Bodies in the Production of Rust.—L. Lindet.—Already noticed.

The Alcoyl-allyl Ketones.—E. E. Blaise.—Already noticed.

Migration of the Ethylenic Bond of the Alcoyl-allyl Ketones.—E. E. Blaise.—Already noticed.

Oxidation of Acetol.—André Kling.—Already noticed.

Constitution of Cyanide of Allyl.—R. Lespieau.—When we leave bromide of allyl, cyanide of potassium, and water in contact for a month at the ordinary temperature, we obtain a nitrile, viz., cyanide of allyl, $\text{C}_4\text{H}_5\text{N}$, to which it seems natural to attribute the formula $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CN}$. Still, at the present time most text-books of chemistry give cyanide of allyl as $\text{CH}_3-\text{CH}=\text{CH}-\text{CN}$, a formula first proposed by Kekulé. The author thinks that, in this paper, he has shown that it is necessary to return to the first formula.

The Hydrosulphites of the Aromatic Bases.—A. L. Lumière and A. Seyewetz.—The possibility of obtaining pure hydrosulphite of soda has enabled the authors to prepare various compounds with certain aromatic bases, which appear to be hydrosulphites of these bases. The compounds described were prepared particularly with regard to their properties as photographic developers. The preparations were—(1) Hydrosulphite of diamidophenol; (2) hydrosulphite of diamidoresorcin; and (3) hydro-

sulphite of triamidophenol. Hydrosulphite of paraphenylenediamine and of the aromatic monamines were also prepared. On the other hand, the simple and substituted monamine phenols, such as paramidophenol, did not give similar compounds.

The Nitrophenylcyanamides. — P. Pierron. — The nitrophenylcyanamides are obtained easily by the action of bromide of cyanogen on the corresponding nitranilines when operating in warm hydro-alcoholic solution. The method of procedure varies slightly from one nitraniline to another, according to the more or less great resistance of the base to the cyanised reagent, and according to the sensitiveness of the cyanamide obtained to the action of the hydrobromic acid given off. The bodies obtained have the same general characteristics as the aromatic cyanamides already described by Hoffmann, Voltmer, and others: fairly marked acid properties, easy transformation into monosubstituted ureas under the influence of acids, the existence of a benzoylised derivative, a tendency to polymerisation manifested by the solidification of these cyanamides after they have been kept melted for some time, with the formation of very difficultly fusible bodies.

Synthesis of Alcohols in the Cyclohexane Series. — Paul Sabatier and Alph. Mailhe. — Already noticed.

Correction on the Subject of Azodiphenylmethane. — P. Freundler. — The author finds, in a continuation of his research on the purification of benzene-o-azo-benzyl alcohol by distillation, that the product which he looked upon as azodiphenylmethane was in reality a molecular combination of azobenzene and phenylindazol.

Research on the Action exercised by different Physical and Chemical Agents on the Gluten of Wheat Flour. Estimation of this Element. — E. Fleurent. — As a result of a long research, the author concludes that chemical analysis has shown that gluten is a definite element of wheat flour, and that its mechanical extraction can be performed integrally and without loss. Distilled water and chloride and sulphate of calcium cause a loss in the estimation of gluten; prolonged washing also causes a loss of weight, and this loss is such as to bring the composition to 25 of glutenine and 75 of gliadine.

Estimation of Phosphoric Acid in Alimentary Substances. — E. Fleurent. — Inserted in full.

Constitution of Ricinine. — L. Maquenne and L. Philippe. — Already noticed.

Coloured Reaction of Cotton-seed Oil. — G. Halphen. — Inserted in full.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Reclaiming Waste Rubber. I should be glad if any reader could give me a few hints on reclaiming indiarubber from waste tyres, &c., or name good book on the subject. — WASTE RUBBER.

ST. PAUL'S SCHOOL, West Kensington. — An EXAMINATION will be held at the above School on Tuesday, September 5th, 1904, and on the following days, for filling up about Twenty Vacancies on the Foundation. — Full particulars of the Examination can be obtained on application to the Bursar

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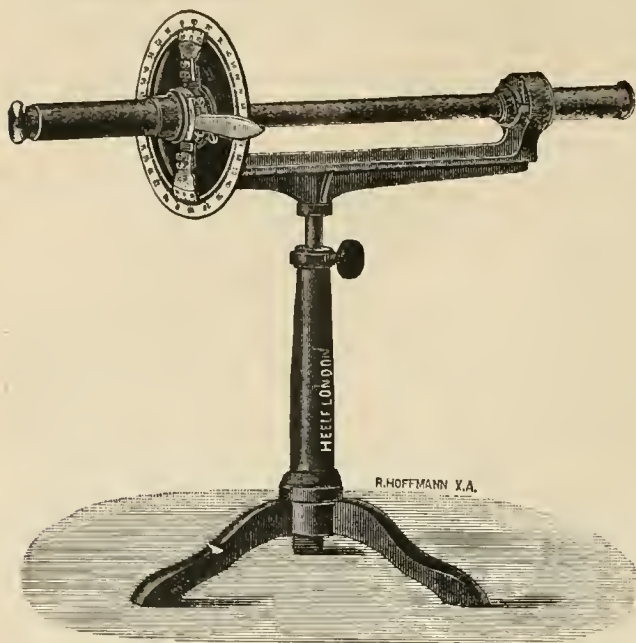
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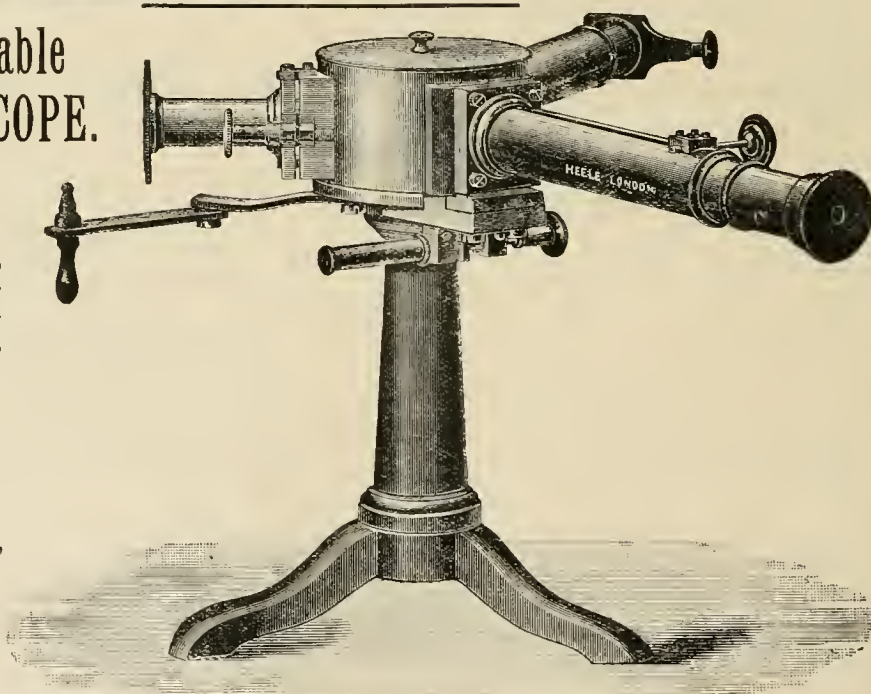
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THE CHEMICAL NEWS.

VOL. XCII., No. 2381.

THORIANITE, A NEW MINERAL FROM CEYLON.*

By WYNDHAM R. DUNSTAN, M.A., LL.D., F.R.S.,

and
G. S. BLAKE, A.R.S.M.,

Assistant in the Scientific and Technical Department of the
Imperial Institute.

THE mineral which forms the subject of this paper was collected in Ceylon during the progress of the mineral survey of the island, which was commenced in 1903, under Professor Dunstan's supervision, with the principal object of determining the extent to which economic minerals, such as graphite, mica, &c. occur, and if possible of discovering other minerals of commercial importance. The minerals collected by Mr. A. K. Coomaraswamy and Mr. James Parsons, the officers entrusted with the survey in Ceylon, are submitted to examination and analysis in the Scientific and Technical Department of the Imperial Institute, and are subsequently subjected to such technical trials as may be necessary in order to ascertain their precise uses and to determine their value.

Among the materials thus received from Ceylon at the Imperial Institute was a small quantity of a heavy black mineral occurring chiefly in small roughly cubical crystals. This mineral was, in the first instance, furnished to the officers of the mineral survey by Mr. W. D. Holland, who believed it to be uraninite or pitchblende. He had previously sent specimens to several persons in this country under this name.

A chemical examination of the small specimen received at the Imperial Institute showed, however, that the mineral contained a large proportion of thorium in the form of the dioxide (thoria) and only a small proportion of uranium. It was evident that this was a new mineral chiefly composed of uncombined thoria (ThO_2). Pending the arrival of more material to enable a further examination of its properties to be made, a preliminary account of its composition and properties was communicated by one of us to *Nature* (March 30, 1904, p. 510), and the name *thorianite* was suggested for the substance, which contained at least 75 per cent of thoria.

It was also stated that the mineral was radio-active and that it apparently contained helium, points which would be made the subject of further investigation.

The publication of these results was followed by a communication to *Nature* (April 7, 1904, p. 533), from Sir W. Ramsay, who announced that he had purchased 6 cwt. of the mineral from Mr. Holland some months previously and had been engaged in its examination. He was unable to confirm the statement that it contained thoria, but announced that it had furnished considerable quantities of helium. In a second communication to *Nature* (April 14, 1904, p. 559), Sir W. Ramsay modified the statement he had previously made that the mineral contained practically no thorium.

Further small supplies of the mineral having since been received at the Imperial Institute, we have been enabled to confirm the conclusion first arrived at that the substance is chiefly composed of thoria, and we now desire to bring before the Royal Society an account of this remarkable new mineral, for which the name *thorianite* is appropriate.

A general account of the composition, properties, and uses of *thorianite* is included in Professor Dunstan's official "Reports on the Results of the Mineral Survey in Ceylon, 1903-4," which was issued as a Parliamentary Paper (Cd 2341) in January, 1905.

Occurrence of Thorianite in Ceylon.

The following account of the occurrence of the mineral, at first supposed to be "uraninite," has been given in official reports by Mr. A. K. Coomaraswamy, B.Sc., the Director of the Mineral Survey in Ceylon.

"Mr. Holland of Dikmukulana has for long taken an interest in local mineralogy, amongst other things obtaining specimens of 'nampu' (gem-bearing gravels) from as many localities as possible by offering a small reward to the native 'gemmers' who bring it. It is difficult to persuade the native that gems are not required or to get him to reveal the true source of 'nampu.' These difficulties overcome, the examination of 'nampus' is an ideal method of gaining a knowledge of heavy minerals of any district. Early in 1903 Mr. Holland obtained 'uraninite' amongst his samples and was gradually able to get as much as 6 cwt. brought to him along with other stuff. This material was sent to England and sold to Sir W. Ramsay at the rate of £50 for 6 cwt. Subsequently Mr. Holland induced a native to show him the source of the material, and finding that some quantity occurred, he took out a prospecting license in the full belief that the locality was Crown land.

"Thorianite, together with a mineral regarded as thorite, and a number of other heavy minerals, is found near Kondurugala, Bambarabotuwa, Province of Sabaragamuwa. The principal deposit occurs in and near the bed of the upper part of the Kuda Pandi-oia, a small stream, which at first occupying a small north-west and south-east strike valley north of the Hopewell-Hapugastenna bridge path, turns through nearly a right angle and joins the Maha Pandi-oia a little below the same path. In the bed of the Kuda Pandi-oia, and in a small 'deniya' swamp just below the swamp, the thorianite is to be obtained in considerable abundance. It could not be discovered *in situ*, but it can hardly be doubted that it is derived from some rock outcropping not far distant from the highest part of the little stream; the stream is so small that after a few days of drought (not very usual in this wet district) no running water is met with above the camp. The matrix is no doubt a rock of granitic type similar to those containing zircon, allanite, &c., which have been met with elsewhere in the Balangoda district, intrusive in the Charnockite series, and classed as belonging to the Balangoda group. Of these rocks the largest exposure (a narrow lenticular mass two miles or more in length) is that of zircon granite on Massena estate (six miles); the rock consists of feldspars, quartz, biotite, zircon, and ilmenite; smaller exposures of zircon granite are found on Herimitigala (eight miles) and Hopewell estates (15 miles); at Denegama bridge, on the road between Balangoda and Belihul-oia, and near the 91st milepost on the same road. There are also similar granites without accessory minerals exposed—e.g., on the main road about a mile below Balangoda. The allanite-granite, or pegmatite, is best seen on Lower Denegama estate, where it occurs as a dyke 3 or 4 feet thick, forming a conspicuous ledge in the bed of the stream which runs through that part of the estate. The rock is composed of feldspars (chiefly orthoclase), quartz, biotite, and allanite. The allanite forms thin tubular idiomorphic and larger irregular crystals, the biggest having a greatest diameter of 3 inches. Almost identical rocks occur (1) in the Weweldola on Dikmukulana estate (11 miles), and (2) at Weligepola (9 miles). It is important to observe that a pegmatite rock, composed mainly of pink orthoclase, quartz, and biotite, with accessory apatite, tourmaline, ilmenite, &c., has been observed on Ambalawa estate, Gampola ("Spolia Zeylanica," vol. i., part 4, 1904), containing, in addition to the above-named minerals, a few cubic crystals of a black mineral at first regarded as uraninite, but which is almost certainly thorianite.

"To return to the Kondurugala locality, the thorianite is probably derived from a granitic rock with no very large

* A Paper read before the Royal Society, May 18, 1905.

* The distances are quoted from Balangoda.

outcrop, but in which it occurs in considerable abundance; perhaps together with the zircon, thorite, and ilmenite, which quite possibly, however, occur separately in other rocks of a similar character. The outcrop of this rock could not be discovered owing to the dense jungle and thick soil and landslips; rock (mainly decomposed granulate) is indeed exposed at several points in the beds of the Kuda Pandi-oya and of the small streams joining it, but any search for the outcrop of a particular rock in the adjoining jungle could only be expected to succeed at the cost of a large expenditure of time and money, and might even then result in failure.

"There is a large area, including at least the whole of Sabaragamuwa and parts of the central, western, and southern provinces, wherein this or other rare heavy minerals may be looked for.

"It is unlikely that any very extensive deposit of any of these rare heavy minerals will be found, but they may be expected to occur at various points in moderate amounts. In the Kuda Pandi-oya valley a total of 5 tons might, perhaps, be obtained; from the Alupola-dola or the Kuda-oya I doubt if half a ton could be profitably extracted, but these estimates are quite uncertain. The Gampola occurrence is quite without commercial value. The total amount actually obtained in Bambarabotuwa, so far, does not exceed 15 cwt. In the immediate neighbourhood of Kondurugala the Walaweduwa jungle seems the most favourable district for investigation. An examination of the Ratganga valley towards the west showed that thorianite is absent there, and that even zircon is very scarce; but on the north-east one or two heavy minerals not yet determined were actually obtained in the southern part of the Walaweduwa Crown Forest Reserve, and further work on that side of Kondurugala might be useful. It must be mentioned, however, that the district is a very wet one, the jungles swarming with leeches; it is also very inaccessible, provisions and camping effects having to be carried fully 20 miles from Balangoda. Camping in these jungles is absolutely useless except in fine weather; and in the absence of a detailed map observations cannot be very accurately set down.

"Since August, 1904, a small deposit of the mineral provisionally identified as thorite was discovered at Durayakanda, South of Gilimale, about six miles from Ratnapura.

"A rather amount of 1200 lbs. of thorianite has since been obtained from Bambarabotuwa."

Description of Thorianite.

Thorianite, as it occurs naturally, is often associated with other minerals, and is not easy to obtain in a completely separate condition.

Dr. J. W. Evans has made a preliminary examination of the crystallographic characters, and intends to further study this subject. It may be stated now that the mineral occurs in small cube-like crystals up to nearly a centimetre in diameter, the largest so far seen measuring rather more than 8 m.m. In most specimens the colour is a dull grey or slightly brownish black, but those crystals which have not suffered from attrition in the streams are a jet black with a bright resinous or pitchy lustre. The difference may be attributed partly to the grinding of the surface and partly to superficial chemical changes. The mineral thus differs from uraninite or pitchblende, which usually occurs massive, and not obviously crystalline. The streak furnished by uraninite is brown with a tinge of green.

By transmitted light the mineral is opaque except in thin sections.

The double refraction is very low. The refractive index probably exceeds 1.8.

The only faces that are ordinarily developed on the crystals of thorianite are apparently those of the cube. These have a very uneven surface, especially in specimens that have not suffered much from attrition or alteration. This character of the surface is mainly the result of the

development of a number of small vicinal faces. In some cases larger faces of similar character are present, meeting at very obtuse re-entrant or salient angles, and reminding one of those seen in some crystals of fluorspar. In other crystals the faces show a more or less irregular curvature.

The indefinite character of the surface prevents any accurate determination of the angles. The goniometric readings vary 2 or 3 degrees on either side of 90 degrees, according to the portions of the surface from which the image is reflected, but there is in most cases no satisfactory evidence that the faces as a whole are not virtually at right angles. Some crystals, however, appear to be distorted and have angles differing from a right angle by as much as 5 degrees or even more.

Occasionally twin crystals are met with, and these are of some interest. They are interpenetrant twins on a face of the octahedron as twinning plane, and one of the diagonals of the cube as twinning axis, exactly similar to those of fluorspar. As in the case of that mineral the coigns of one cube project as pyramids on an isosceles triangular base on the face of the other. Sometimes the compound form is almost completely regular, four edges of each cube meeting at one point or approximately so at both ends of the common diagonal that forms the twinning axis; at other times the composition is more irregular, and a number of coigns project from the faces of a cube in such a manner that, though the faces of one coign are parallel to those of another, they are not in the same plane. In these forms the twinning axis and plane are the same for all the coigns, even when there is more than one projecting from the same face, the more acute point of the pyramid pointing to the coign of the cube from which the twinning axis emerges. The diagonal which constitutes this axis has therefore crystallographic characters different from those of the other three diagonals, about which this twinning cannot apparently take place, and the symmetry of the crystal must be considered as rather rhombohedral than cubic, although the angles are apparently right angles. The same considerations would apply to fluorspar, in which case the essentially rhombohedral character of its symmetry is confirmed by the occurrence of crystals in which only those faces of the four faced cube or tetrakis hexahedron $\{310\}$ are developed, in which the finite intercepts are of opposite signs. These faces may be represented by the symbol $\{310\}$, and are those which bevel the edges that do not pass through the coigns at the ends of the unique diagonal. They together form a scalenohedron, which is in fact the scalenohedron $\{1342\}$ of the rhombohedral system, assuming the cube as the fundamental rhombohedron. ("Lehrbuch der reinen und Angewandten Krystallographie," 1830, p. 178, Fig. 572).

A similar scalenohedron $\{210\}$ or $\{1231\}$ is repeatedly met with in crystals of halite. (F. von Kobell, "Über Merkwürdige Krystalle von Steinsalz," *Journ. für Prakt. Chemie*, 1861, vol. lxxxiv., p. 420; K. André, "Über Steinsalz Krystalle von hexagonal-rhomböedrischer Pseudosymmetrie aus Sicilien," *Centralb. für Mineralogie*, 1904, p. 88).

It is interesting to notice that chabazite, which is cubic in general appearance, but really rhombohedral, having its angles differing from right angles by nearly 5 degrees, twins in exactly the same manner as fluorspar and thorianite.

The inference that thorianite is essentially rhombohedral in character is confirmed by the observation that in sections cut perpendicular to the twinning axis the substance is practically isotropic.

Thorianite shows no definite cleavage, but the mineral is traversed by irregular cracks which appear to follow the direction of the basal plane more frequently than any other. On fracture, it shows an irregular surface, which is more or less conchoidal on a small scale.

The hardness of the mineral is nearly 7, which distinguishes it at once from uraninite with a hardness of 5.5.

Under the blowpipe thorianite is infusible. It decrepitates, and if raised to a sufficiently high temperature is highly incandescent.

It is sometimes associated in rolled fragments with a smooth, yellow-brown, apparently amorphous material, of hardness 6, which envelopes it or forms a rounded deposit on its faces. This substance is reddish-yellow in colour when viewed in thin sections by transmitted light. Zircon also sometimes occurs intergrown with thorianite.

The density of different specimens of thorianite varies between 8 to 9.5 and 9.7. The higher numbers probably represent the density of the actual mineral, which in some cases exhibits cavities partially filled with a yellow ochreous material and also inclusions of zircon, one of the minerals generally associated with thorianite, and these associated minerals, especially those which contain thorium, will be investigated if a sufficient quantity can be obtained separated from thorianite.

The mineral is easily powdered and then dissolves readily in strong nitric acid or in diluted sulphuric acid, with evolution of a gas which is chiefly helium. Thorianite is scarcely attacked by hydrochloric acid.

Thorianite is highly radio-active, and, in fact, may prove to be one of the most radio-active of minerals. The cause of this radio-activity is referred to below.

(To be continued).

THE COMPLETE ANALYSIS OF LEAD ORES.

By J. A. MULLER.

I. The method of estimating lead in galena, first proposed by F. Stolba and improved by Fr. Mohr ("Fresenius," 6th French edition, p. 975), has not given me satisfactory results. The determination of lead in its ores can be effected much more accurately by weighing this element in the state of sulphide, as has been shown in a previous paper.

The following is the best method, according to experiments I have made on this subject, for estimating the lead and also the other elements and compounds which accompany lead in its ores.

To about 1.5 grms. of the finely powdered ore, weighed accurately in a covered platinum crucible, we add gradually 10 c.c. of nitric acid (density = 1.33) and leave the mixture in a warm place for twelve hours. Exhaust the residue—from which the greater portion of the excess of acid is removed—in the same crucible with warm water, and filter through a small filter. Without troubling whether the filtrate is a little cloudy or not, we add 40 c.c. of a 10 per cent solution of acetate of soda, bring the mixture to boiling, and filter to separate the ferruginous precipitate.

In the filtrate the silver is precipitated by a slight excess of hydrochloric acid. As for the ferruginous precipitate, it is dissolved in hydrochloric acid, and the solution added to the product of exhaustion, at about 80°, of the residue insoluble in water, by about 60 c.c. of a mixture of equal volumes of fuming hydrochloric acid and water. After washing with boiling water we add to the clear filtrate that resulting from the filtration of the AgCl, and enough water to make 1.5 litres of liquid, which is heated to about 70°, and saturated with H₂S, then let stand for a day, and filtered.

The portion insoluble in hydrochloric acid contains the quartz, the insoluble silicates, and the greater part of the sulphate of baryta. After calcination and weighing, we can estimate the silica by difference by treating with hydrofluoric acid.

As for the precipitate formed by sulphuretted hydrogen, it is filtered on a tared filter, washed, and detached as completely as possible from the filter, and the aqueous magma, containing about 50 c.c. of water, treated with 6 c.c. of a concentrated solution of sulphurised ammonium sulphide (or, in the presence of copper, with sulphurised sulphide of sodium), at a temperature below boiling; the liquid is decanted on to a tared filter-paper, and the residue again treated three or four times, hot, with a small quantity

of water containing 0.5 c.c. of the sulphurised sulphide; finally, we wash with pure water, and, after having changed the recipient, with alcohol, &c., the precipitate is dried *in vacuo* over sulphuric acid, and weighed.

The precipitate of sulphide of lead may contain cupric sulphide and also a small quantity of sulphide of silver. This latter metal is estimated by treating an aliquot part of the precipitate with iron at a red heat in the presence of an alkali, and submitting the metallic button obtained to cupellation. Traces of gold may be also looked for by cupellation, but the ore itself must be used. Take up the small globule of silver with nitric acid, and the gold remains as residue. As for the copper, if present, it must be separated from the lead by transforming an aliquot part of the precipitate of sulphide into sulphate by means of nitric acid, then after the addition of a little sulphuric acid and a drop of hydrochloric, separate the soluble sulphate of copper in a mixture of alcohol and water.

The sulphurous solution already obtained contains arsenic and antimony; it is acidulated slightly with hydrochloric acid, then filtered immediately, and the precipitate washed with water, alcohol, &c.; the precipitate almost free from sulphur is then dried, and treated at boiling temperature with a mixture of two volumes of fuming hydrochloric acid and one volume of water (about 60 c.c. altogether). In the dilute hydrochloric solution the antimony is precipitated in the form of sulphide, and then estimated as such.

As for the insoluble sulphide of arsenic, mixed with a little sulphur, it is dissolved in boiling nitric acid (density = 1.33) and the arsenic estimated in the form of ammonio-magnesian arseniate (AsO₄NH₄Mg + 0.5H₂O at 102°). It is necessary to re-dissolve the precipitated arseniate and to re-precipitate it, adding only a small quantity of magnesian mixture. In the mother-liquors from the precipitates of arseniate there are still small quantities of arsenic and antimony, which may be precipitated by H₂S in acid solution, and separated as described above.

The liquid separated by filtration from the precipitated PbS, &c., may still contain iron, zinc, and calcium. The sulphuretted hydrogen is driven off by boiling, and the solution is then concentrated down to one-third of its volume; it is oxidised by means of bromine, and made alkaline with ammonia; the precipitate of Fe₂O₃ formed should be re-dissolved in the smallest possible quantity of hydrochloric acid to separate from it the sulphate of baryta which may be present, then the solution is re-precipitated by ammonia in the presence of a little chloride of ammonium. The zinc is estimated in the form of sulphide, and the calcium as oxide after precipitation as oxalate. After the separation of this latter metal the filtered liquid is evaporated to dryness, the residue is calcined and taken up with a little dilute hydrochloric acid to separate a further possible quantity of sulphate of barium.

11. The bodies generally accompanying galena in its ores are, besides the products of the decomposition of the sulphide of lead—such as anglesite and cerussite—quartz and silicates, blende, calcite, fluorite, barytine, and pyrites; finally, in certain varieties we also meet with arsenic and antimony. Argentiferous galenas contain from 0.01 to 1.0 per cent of silver.

For the purpose of checking the method of analysis just described, I made an intimate mixture of the following porphyrised compounds:—Crystals of pyrites (without copper and with 46.44 per cent Fe), 0.685 gm.; pure fluorine, 1.195 grms.; pure quartz, 0.649 gm.; pure crystallised sulphate of baryta, 3.217 grms.; pure crystallised carbonate of lime, 0.313 gm.; sulphide of zinc at 97 per cent sulphur, 0.714 gm.; pure sulphide of arsenic, 0.183 gm.; pure sulphide of antimony, 0.276 gm.; sulphide of silver precipitated and dried *in vacuo*, 0.337 gm. The six latter bodies were obtained artificially.

Two assays, A and B, were made; in the former we analysed a mixture composed of 0.5956 gm. PbS at 0.15 per cent of water and 0.6122 gm. of the above mixture; in the latter the sample analysed consisted of 0.7034 gm.,

of the same sulphide of lead and 0.6073 grm. of the preceding mixture.

The following results were obtained:—

	Assay A.		Assay B.	
	Calculated. Grm.	Found. Grm.	Calculated. Grm.	Found. Grm.
Pb ..	0.5148	0.5197	0.6081	0.6135
Ca ..	0.0597	0.0606	0.0592	0.0590
Zn ..	0.0376	0.0370	0.0373	0.0372
Fe ..	0.0257	0.0281	0.0255	0.0285
As ..	0.0093	0.0075	0.0092	0.0085
Sb ..	0.0159	0.0146	0.0158	0.0154
Ag ..	0.0237	0.0203	0.0235	0.0224
LiO ₂ ..	0.0525	0.0514	0.0520	0.0498
BaSO ₄ ..	0.2600	0.2631	0.2579	0.2525

—*Bull. Soc. Chim.*, Series 3, vol. xxxi., No. 24.

THE

ESTIMATION OF PHOSPHORIC ACID IN FOODS.

By E. FLEURENT.

THE total quantity of phosphorus entering into the composition of the animal and vegetable materials constituting our food is an important factor in the alimentary value of these products. Up to quite recently the determination of this element was effected by starting with the ashes obtained by the incineration of a known weight of the material in question, either with or without a certain quantity of caustic lime, and finally estimating the pyrophosphate of magnesia obtained by the calcination of the precipitated ammonio-magnesian phosphate. M. Garola ("International Congress of Applied Chemistry, 1896," vol. ii., p. 161) has shown by means of experiments with wheat, that the operation carried out in this manner leads to the loss of a considerable proportion of the phosphorus (31 per cent of the amount estimated) on account of the reduction of the acid phosphates by the carbon of the organic matter,* and he proposed to use Kjeldahl's method for the destruction of this latter substance, as generally used in laboratories. In practice the destruction of the organic matter by this method is very long, and therefore it becomes necessary to operate only on small samples, say, for 2 to 4 grms.

We next meet with the following drawback:—The phosphorus being only a very small part of the substance to be examined, the precipitation in the form of ammonio-magnesian phosphate is no longer convenient, as it leaves as the residue in the final calcination an amount of pyrophosphate too small to be used with safety in the calculation of the percentage present. M. Garola has got round this difficulty by precipitating the phosphoric acid with molybdate of ammonia, and weighing, with certain precautions which he points out, the phospho-molybdate obtained, and then calculating the phosphoric acid by means of the coefficient 3.54, the invariability of which he has made certain of under the conditions of the experiment.

The method devised by M. Garola leads to exact results provided it is followed with the greatest care in all its details. It sometimes happens, however, as I have found in practice, that in spite of all the attention that may be given to the operation the invariability of the coefficient 3.54 is not always certain, so that there is this objection to the method, that this variability of the coefficient and the small amount of the sample taken may lead finally to an important multiplication of the errors inherent to all analytical methods.

To avoid these various drawbacks, I have for some years past used a method in my own laboratory which, based on the destruction of the organic matter by the successive

use of nitric and sulphuric acids, enables me to work on 10 or 20 grms. of material, according to its richness in phosphorus, and thus in every case to weigh a proportion of pyrophosphate of magnesia always sufficient to ensure the correctness of the analytical calculations.

The following is the manner in which this method must be applied:—If the material contains an excessive proportion of moisture it is previously dried and reduced to powder; if not, it is used in the condition it happens to be in, in a state of division suitable for the attack. We then weigh 10 or 20 grms. which are placed in a conical flask of 300 c.c. capacity, and covered with 50 to 100 c.c. of fuming nitric acid of 1.48 density. We heat carefully at first, gently agitating the flask with a circular movement, so as to break down the froth which is formed by the abundant disengagement of gas, and to prevent the mass running over. We then continue the evaporation until only a few m.m. of liquid remain at the bottom of the flask, and finally complete the evaporation to dryness in the oven at 110 to 120°. On this residue we pour 15 to 20 c.c. of sulphuric acid (two-thirds acid at 66°, and one-third fuming acid), add one drop of mercury, and finish the attack in the manner described by Kjeldahl.

The attack finished, we dilute carefully with distilled water, and saturate the sulphuric acid with ammonia, taking care to keep the mixture cool. Transfer to a precipitating glass, using the following mixture as wash-water:—Ammonia, 500 c.c.; NH₄Cl, 200 c.c.; water to 1 litre.

We then precipitate with magnesia mixture, and complete the estimation in the ordinary manner.

The following figures, obtained in duplicate on various animal and vegetable food materials, show the sensitiveness of the method and the concordance it is possible to obtain:—

	Moisture.	P ₂ O ₅ per cent on the dry material.	
		I.	II.
Haricot flour ..	18.14	1.077	1.079
Camembert cheese ..	46.96	1.102	1.105
Yolk of egg ..	49.06	2.843	2.845
Lean beef ..	74.00	1.894	1.904
Brie cheese ..	53.24	1.272	1.273
Gruyère cheese ..	35.15	2.475	2.495
Wheat-flour (70 per cent extraction) ..	15.46	0.357	0.344
Cabbage leaves ..	89.00	1.625	1.621

—*Bull. Soc. Chim.*, Series 3, vol. xxxiii., No. 1.

THE

CONSTITUTION OF THE HYDROSULPHITES.

By MAURICE PRUD'HOMME.

A SEALED packet was deposited by Em. Zundel, manufacturer of muslins, of Moscow, at the Société Industrielle de Mulhouse, on December 15, 1902. It describes the interesting observation that the hydrosulphites unite with formic aldehyde, giving crystallisable double compounds, analogous with those formed by the bisulphites with the aldehydes. These bodies are much more stable than the simple hydrosulphites, even than the slightly soluble hydrosulphites, such as that of zinc. It is only under the action of steam at 100° that the double hydrosulphite of soda-formaldehyde, for example, splits up into formic aldehyde and hydrosulphite of soda, which, in the nascent state, acts as a reducing agent of uncommon energy.

The chemists belonging to the firm of Em. Zundel, Messrs. Schwartz, Baumann, Sunder, and Thesmar, have utilised the properties of the bodies discovered by them for the direct fixation of indigo, and for the production of perfect white prints on tissues tinted with insoluble azoic colouring materials, such as paranitraniline red, *a*-naphthylamine garnet, &c.

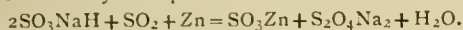
* In a research I am now carrying on in my laboratory I am going on to the mechanism of this loss.

Quite recently Messrs. Baumann, Thesmar, and Frossard presented to the Société Industrielle de Mulhouse (Nov. 9, 1904) a paper on the constitution of formaldehyde hydrosulphite, of which we will discuss the essential points.

Hydrosulphite of soda is prepared from bisulphite of soda, sulphuric acid, and zinc in the presence of ice. When the reaction is completed the whole of the zinc is precipitated by means of Solvay's soda, sifted into the liquor. When the latter is neutral it is passed to the filter-press, and precipitated with sea-salt. The precipitate is filtered, pressed strongly, and mixed with the necessary quantity of formaldehyde at 40 per cent.

On cooling, the liquor gave an abundant crystallisation of what seemed to be a well-defined product. Nevertheless, by means of fractional crystallisations in dilute alcohol, we are able to divide it into two bodies, one of which is the bisulphite of soda-formaldehyde, $\text{SO}_3\text{NaH} + \text{CH}_2\text{O} + \text{H}_2\text{O}$, and the other the bihydrosulphite of soda-formaldehyde, $\text{SO}_2\text{NaH} + \text{CH}_2\text{O} + 2\text{H}_2\text{O}$, which occurs in the form of magnificent crystals, apparently belonging to the clinorhombic system.

Messrs. A. Bernthsen and M. Bazlen in a recent paper (*Berichte*, 1900, vol. xxxiii., p. 126; and *Bull. Soc. Chim.*, 1900, [3], vol. xxiv., p. 404) on hydrosulphite of soda, prepared by means of a mixture of bisulphite of soda, sulphurous acid, and zinc, and precipitated by sea-salt, deduced from their analyses the constitutional formula $\text{S}_2\text{O}_4\text{Na}_2 + 2\text{H}_2\text{O}$ for hydrosulphite of soda, and explained its formation by the equation—



We know, on the other hand, that Schutzenberger has always upheld the formula SO_2NaH for hydrosulphite of soda. This is now absolutely confirmed by the work of the Moscow chemists, who have definitely established that M. Bernthsen's salt is not, as he supposed, the neutral hydrosulphite of soda in a state of purity, but a mixture of 1 molecule of bisulphite of soda and 1 molecule of the true acid hydrosulphite discovered and described by Schutzenberger.

With the work of Messrs. Baumann, Thesmar, and Frossard is connected directly the beautiful experiment of Moissan (*Bull. Soc. Chim.*, 1903, [3], vol. xxix., p. 10) on the reciprocal action of the alkaline or alkaline-earth hydrides and sulphurous anhydride, which may be formulated $2\text{KH} + 2\text{SO}_2 = \text{S}_2\text{O}_4\text{K}_2 + \text{H}_2$.

The white salt thus obtained, taken up with a small quantity of water free from oxygen, gives, by simple evaporation away from the air, fine transparent needles or small acicular crystals grouped together in stars, and gives the characteristic reducing reactions of the alkaline hydrosulphites.

The salt, $\text{S}_2\text{O}_4\text{K}_2$, thus hydrolyses in contact with water; one of the terms of the reaction being the bihydrosulphite, which we know has for its formula SO_2KH , the other must necessarily be bisulphite of potassium according to the equation $\text{S}_2\text{O}_4\text{K}_2 + \text{H}_2\text{O} = \text{SO}_2\text{KH} + \text{SO}_3\text{KH}$. This fact agrees with the formation of two distinct crystalline forms.

M. Bernthsen's salt, $\text{S}_2\text{O}_4\text{Na}_2 + 2\text{H}_2\text{O}$, admitting its existence as a chemical body, would be a hydrate of M. Moissan's corresponding salt, $\text{S}_2\text{O}_4\text{Na}_2$. As it is isolated by precipitation with sea-salt, the contact with the saline solution might very well bring about hydrolysis, and cause the formation of a body with a certain stability. But in the presence of pure water it should be hydrolysed like M. Moissan's salt, and decomposed into its elements. If we react with zinc on its aqueous solution, the free bisulphite should then give rise to a further quantity of bihydrosulphite.

Titration with iodine, with or without carbonate of soda, as described by the Moscow chemists, would enable us to make certain of the progress of the reaction and to observe the action of the hydrolysis.

The crystalline bodies of the type $\text{S}_2\text{O}_4\text{M}_2$, obtained by

M. Moissan by the dry way, do not raise the same doubts as the compound $\text{S}_2\text{O}_4\text{Na}_2 + 2\text{H}_2\text{O}$ of M. Bernthsen, and should be looked upon as the neutral salts of a new sulphuric acid, $\text{S}_2\text{O}_4\text{H}_2$.—*Bull. Soc. Chim.*, Series 3, vol. xxxiii., No. 2.

MEETING OF THE BRITISH ASSOCIATION IN SOUTH AFRICA.

THE arrangements for the forthcoming meeting of the British Association in South Africa have now been completed, and Mr. Silva White, the Assistant Secretary of the Association, sailed for Cape Town in the *Walmer Castle* on Saturday, July 1. The number of members who will proceed to South Africa to attend the meeting is 385, and of these no less than 276 members have intimated their intention to visit the Victoria Falls at the conclusion of the ordinary work of the Association. The official party, consisting of leading representatives of Science and guests of the Association, with the General and Sectional Officers for this meeting and the President, numbers 140 in all, and will sail by the *Saxon* on July 29. Most of the other members will proceed to the meeting by the *Durham Castle* and the *Kildonan Castle*, both of which sail on July 22.

In a previous article (*CHEMICAL NEWS*, xci., p. 52) the local arrangements for the meeting were described. There will be receptions and social functions, excursions, &c., at Cape Town, Durban, Pietermaritzburg, Johannesburg, Kimberley, and Bulawayo. The Central Organising Committee for South Africa (chairman, Sir David Gill, K.C.B., F.R.S.; hon. secretary, Dr. Gilchrist) has carried out the co-ordinating work of the programme. The lists of local committees and sub-committees contain nearly one thousand names, from which it may be concluded that much interest is taken in the meeting.

As already mentioned, lectures of a popular character will be delivered at the chief towns visited. These lectures have now been definitely arranged as follows:—

Cape Town.—W. J. Burchell's discoveries in South Africa. Prof. Poulton; some surface actions of fluids, Mr. C. V. Boys.

Durban.—Mountains: the highest Himalaya, Mr. D. Freshfield.

Pietermaritzburg.—Sleeping-sickness, Colonel D. Bruce. *Johannesburg*.—Distribution of power, Prof. Ayrton; steel as an igneous rock, Prof. Arnold.

Pretoria.—Fly-borne diseases, malaria, sleeping-sickness, &c., Mr. A. E. Shipley.

Bloemfontein.—The Milky Way and the clouds of Magellan, Mr. A. R. Hinks.

Kimberley.—Diamonds, Sir William Crookes; bearing of engineering on mining, Prof. Porter.

Bulawayo.—Zimbabwe, Mr. Randall MacIver.

The President's Address to the Association will be delivered at Cape Town on August 15, and at Johannesburg on August 30. Mr. G. W. Lamplugh's report on the geology of the Victoria Falls will take the form of an afternoon Address to Section C at Johannesburg.

Subjoined is a draft programme of the work of the sections:—

Section A (Mathematics and Physics).—*Cape Town*: President's address; progress of the arc of meridian and geodetic survey of South Africa, Sir D. Gill; to what extent can the ether affect the motion of matter? Prof. J. Larmor; observations of atmospheric electricity in South Africa, Prof. Beattie and Mr. Lyle; leak of electricity from certain heated substances, Prof. Beattie; the foundations of the kinetic theory of gases, Mr. Burbury; application of the kinetic theory of nebulae, Mr. J. H. Jeans; radiation at low temperatures, Dr. J. T. Bottomley. There will also probably be communications from Mr. Hough on tides, and from Dr. Roberts on the Algal variables

Johannesburg: On the teaching of elementary mechanics (jointly with Section L if possible), Prof. J. Perry; on flight, Prof. G. H. Bryan; (1) electrical conductivity in relation to chemical action; (2) magnetic survey of South Africa, Prof. Beattie; report of the seismological committee, Prof. J. Milne; a form of dry Daniel cell, Mr. J. Brown; the strength of winding ropes in mines, Prof. Perry; the experimental foundations of the theory of heat conduction, Dr. C. H. Lees. There will probably be a communication from Mr. Sutton on the meteorology of South Africa.

Section B (Chemistry).—Detailed information regarding papers offered by members in South Africa has not yet been received, but the following provisional arrangement has been made:—*Cape Town*: Recent advances in agricultural science, A. D. Hall; vegetable assimilation, Dr. Horace T. Brown; enzyme action, Dr. E. F. Armstrong. These communications are intended to serve as a basis of discussion of agricultural chemical problems. *Johannesburg*: President's address; reports on various aspects of the metallurgy of gold by local experts. Communications by Dr. H. Marshall on the experimental basis of the dissociation hypothesis, and by H. Ingø on the soils of the Transvaal, have been provisionally accepted.

Section C (Geology).—*Cape Town*: Opening remarks by the President; the continent of Africa in relation to the physical history of the earth, Prof. W. J. Sollas; the classification of the Karroo beds of South Africa, Prof. R. Broom; report of the committee on the fauna and flora of the English Trias, J. Lomas; extraordinary daily fluctuations in a Karroo well, Prof. A. Young; and other papers on the Karroo or Trias. *Joint meeting with Section E (Geography)*.—The physical geography of Cape Colony, H. C. Schunke-Holloway; Glacial periods in South Africa, A. W. Rogers; changes of climate as shown by movements of the snow line and upper tree line since Tertiary times, Prof. A. Penck; physiographical subject, Prof. W. M. Davis; Bavarian's Kloof, a contribution to the theory of mountain folds, E. H. L. Schwarz; the Stormberg formation in the Cape Colony, A. L. Du Toit; on the geology of South Victoria Land, H. T. Ferrar. *Johannesburg*: President's address; magnetic segregation of sulphide ores, Dr. A. P. Coleman; marginal phenomena of granite domes, Prof. G. A. J. Cole; relation of the igneous rocks to the crystalline schists, F. P. Mennell; the indicators of the goldfield of Ballarat, Prof. J. W. Gregory; petrographical subject, Prof. R. B. Young; the diamond pipes and fissures of South Africa, H. S. Hargreaves; recent work of the Transvaal Geological Survey, H. Kynaston; the Victoria Falls, G. W. Lamplugh; the great laccolitic intrusions of the Bushveld, Dr. G. A. F. Molengraaff; evidences in the Transvaal of Glacial conditions in permo-Carboniferous times, E. T. Mellor; geological notes on the excursion to Pretoria, A. L. Hall; the great West Rand upthrust, Dr. J. T. Carrick; notes on a sedimentary formation older than the Witwatersrand beds, E. Jorissen; interesting outlines of the Witwatersrand formation, Dr. J. T. Carrick.

Section D (Zoology).—*Cape Town*: President's address; the Triassic reptiles of South Africa, with remarks on the origin of mammals, Dr. Broom; a comparison of the Permian reptiles of Russia with those of South Africa, Prof. Amalitzky; South African scorpions, Dr. Purcell; recent work on gametogenesis and its bearing on theories of heredity, L. Doncaster; the migration of birds, in the southern hemisphere, W. L. Sclater; the ostrich, A. H. Evans. *Johannesburg*: Pearl oysters and pearls, Prof. Herdman; recent discoveries in the South African deep sea, Dr. Gilchrist; cephalopods, Dr. Harmer; the growing-point in vertebrates, Prof. Cleland; South African ticks, Drs. Cooper-Foster and Nuttall.

Section E (Geography).—*Cape Town*: President's address; afforestation of South Africa; the unveiling of the coasts of Africa (lantern views of old maps), H. Yule Oldham; the Ordnance Survey of the United Kingdom, Colonel Johnston; a comparison of the periodicity of the

meteorological conditions of London and Cape Town, Dr. H. R. Mill; Gough Island, Rudmose Brown; terrestrial globes as a necessary adjunct to the teaching of geography, Captain Creak; excursions as a means of teaching geography (lantern), J. Lomas. *Johannesburg*: The evolution of Africa, Dr. J. Scott Keltie; a new rainfall map of Africa, A. J. Herbertson and P. C. Waite; boundaries and areas in Africa, J. Bolton; the physical geography of the Transvaal, Tudor Trevor; notes on the geography of Africa south of the Limpopo, F. S. Watermeyer; the game preserves of the Transvaal, Major Stevenson Hamilton, D.S.O.; the Sikhim, Himalayas, and Tibet, Douglas W. Freshfield; Asiatic subject, Prof. Cordier.

Section G (Engineering).—*Cape Town*: Metcalf on Zambezi Bridge and Rhodesian Railways; ocean turbine boats, Prof. Byles; roller bearings, wire ropes in mines, and probably automobiles. *Johannesburg*: President's address (irrigation); strength of winding ropes in mines, Prof. Perry.

Section H (Anthropology).—*Cape Town*: President's address; the totemism of the Bantu, E. S. Hartland; the musical instruments of the natives of South Africa, Hy. Balfour; American negroes, Miss Pullen-Burry; artificial deformation in Africa, Dr. von Luchan. *Johannesburg*: arts and crafts among the natives of South Africa, Dr. Shoenland; stone implements in South Africa, Mr. Johnstone; bushman paintings with reproductions, Dr. Squire; the affinities of the Hottentots, Dr. von Luschan; the Modjadje, Rev. Reuter; the Bawenda, Rev. Gottschling; report on Zimbabwe, Mr. MacIver; the Basuto, H. E. Mabile.

Section I (Physiology).—*Cape Town*: Discussion on the effect of climate on health, opened by Sir T. Lauder Brunton (Dr. David Ferrier, Prof. McKendrick, Dr. Gregory, Dr. Jasper Anderson, Prof. Bohr, and Dr. J. A. Mitchell will take part); so-called scurvy of South Africa, Dr. Gregory; on plague, Dr. J. A. Mitchell; leprosy in Cape Colony, Dr. A. S. Black; South African drugs, Dr. Moberley; discussion on horse-sickness and allied diseases, opened by Dr. Edington (Dr. Hutcheon, Mr. Du Plessis, Dr. Wm. Robertson, Colonel Bruce, and Prof. Sims Woodhead will take part); stock diseases in South Africa, Dr. Hutcheon; ticks as a means of conveying disease in South Africa, Mr. Lounsbury. *Johannesburg*: President's address; horse-sickness, Dr. Theiler; rinderpest, Dr. G. Turner; a discussion on lung diseases in connection with mining (Dr. Sims Woodhead) is under consideration; nervous diseases, Prof. Ferrier; the life-history of coloured labourers in the Transvaal, Dr. D. Macaulay and Dr. Louis Irvine; dysentery, Colonel Cecil Birt.

Section K (Botany).—*Cape Town*: The present position of our knowledge of seaweeds, Prof. R. W. Phillips; the fossil floras of South Africa, A. C. Seward; educational methods in the teaching of botany, Harold Wager; notes on irrigation farming on the Orange River, F. B. Parkinson. *Johannesburg*: President's address; photography as an aid to æcological research, Prof. F. E. Weiss; the problems of heredity, R. P. Gregory. It is expected that Prof. Engler, Prof. Pearson, and others will contribute papers.

Section L (Educational Science).—*Cape Town*: President's address; the teaching of science, Prof. H. E. Armstrong; the teaching of science in South Africa, Dr. Hahn; rural education, appropriate to colonial life in South Africa, and agriculture, A. D. Hall; the higher education of women in South Africa, Miss Clarke; disabilities of South African school-boys, W. A. Way; Cape education, its difficulties and development, Rev. W. E. C. Clarke. *Johannesburg*: Changes in the Dutch language since its introduction into South Africa, Dr. Brill; education on the veldt, Mr. Corbett; prospects of secondary schools in the Transvaal, Mr. Hope; teaching of agriculture, F. B. Smith; native education, Hobart Houghton; progress of education in the Transvaal, H. Warre Cornish; education in Rhodesia, G. Duthie; a school of forestry, T. R. Simms; the teaching of architecture, R. G. Kirkby; education in the Orange

River Colony, Hugh Gunn; manual instruction in the Transvaal, T. Lowden; recent improvements in the training of infants, with special reference to South Africa, Miss Welldon; discussion with Section A, the teaching of elementary mathematics.—*Nature*.

PROCEEDINGS OF SOCIETIES

PHYSICAL SOCIETY.

Ordinary Meeting, June 30th, 1905.

Dr. R. T. GLAZEBROOK, F.R.S., Past-President in the Chair.

A PAPER ON "The Comparison of Electric Fields by means of an Oscillating Electric Needle" was read by Mr. D. OWEN.

This paper describes experiments which show how an "electric needle" may be used to measure electric fields in a manner similar to that in which a magnetic field is measured by an oscillating magnetic needle. The needles used were cylindrical in form, of aluminium or of brass, and were suspended by quartz fibres three or four inches in length. The couple on the needle when disturbed from the direction of the field is proportional to the square of the field strength. For small displacements the needle vibrates isochronously, the frequency being proportional to the electric force. It may be used in alternating as well as in steady fields, and may be applied to illustrate many of the laws of electrostatics. The disturbing effect of the needle upon the field is considered; in particular its effect when placed in a uniform field. It is shown by experiments that the disturbing effect falls off rapidly with the distance from the needle, and is inappreciable (in the case of a needle $1\frac{1}{2}$ cms. long) at a distance of twice the length of the needle. With regard to the effect of the dimensions of the needle upon the frequency (for given field), while the restoring couple decreases rapidly with decrease of size, yet the moment of inertia decreases more rapidly, so that the smaller the needle the greater the frequency and also the smaller the disturbing effect. The shielding effect of some dielectric materials was examined in the following way:—A needle was suspended centrally in the uniform field between a pair of parallel plates. A thin walled cylinder of the dielectric was placed around the needle, and the shielding action denoted by a fall in frequency of the needle. Glass and mica were found to effect perfect shielding. Ordinary paper shields; but when thoroughly dried by heat the electric field is transmitted undiminished only to fall off to zero after a minute or two's exposure to the air. Dry paper soaked in melted paraffin-wax transmits the field perfectly and for an indefinite time. The paper concludes by pointing out that an electric needle suspended between a pair of parallel plates forms a simple means of measuring high voltages, since the frequency of vibration is simply proportional to the voltage between the plates.

Prof. R. W. Wood read a paper on "The Magneto-Optics of Sodium Vapour and the Rotatory Dispersion Formula."

It has been shown in a previous paper that the vapour of metallic sodium is an ideal substance for investigating the effect of a strong absorption band on the magnetic rotation of the plane of polarisation. The preliminary work was not very satisfactory, as the method employed did not admit of very accurate determinations of the wave-lengths. Improvements in the methods of observation and design of the apparatus have been accompanied by an increase in accuracy, and accurate readings have been obtained for as many as nine different values of λ between D_1 and D_2 . Rotations as great as 1440° (four complete revolutions) have actually been observed, and this with a 10 c.m. column of not very dense vapour in a field of 2000 C.G.S. units. In the present paper the magneto-optics of the

vapour for light travelling along the lines of force are discussed. The sodium was heated in a tube of thin steel, the ends of which projected from the helices of the magnet. It was found that the field strength within the steel tube did not differ greatly from that obtained when glass tubes were used. A short piece of small brass tubing is brazed into one end of the steel tube, through which the steel tube is exhausted. A good vacuum is essential, all traces of rotation disappearing in hydrogen or nitrogen at atmospheric pressure. Light from an arc-lamp made parallel by a lens is passed through a Nicol's prism, the steel tube, and a second Nicol, after which it is brought to a focus upon the slit of a spectroscope by means of a second lens. In the present case, a concave grating of 14 feet radius was used instead of a spectroscope, the observations being made both visually and by means of photography. The paper then describes the phenomena which are presented when the sodium vapour is formed in the magnetic field. In the case of very dense vapours the rotation has been measured over a considerable range of wave lengths, namely, throughout the region comprised between $\lambda = 5840$ and $\lambda = 5922$. The rotation constant of D_2 was found to be about double that of D_1 . Drude, in his "Lehrbuch der Optik," has given two formulæ for the magnetic rotatory dispersion, the first of which, developed from the hypothesis of molecular currents, calls for an anomalous effect on crossing the band, and does not apply to sodium vapour. The second, developed from the Hall-effect hypothesis, predicts rotations of similar sign and equal magnitude for wave-lengths symmetrically situated in the spectrum, with respect to the centre of the absorption-band. It seems likely that the molecular currents play some part, and that the formula built up on the hypothesis of the Hall-effect is incomplete. However, the latter formula represents the rotation outside of the D-lines with great accuracy, while between the lines it gives in some cases a curve which is elevated somewhat above the experimental curve. The paper concludes with an account of the bright-line spectrum produced by magnetic rotation which presents itself when the Nicol's prisms of the apparatus are crossed. The spectrum, which at first could only be seen with difficulty, was finally obtained of such brilliancy that it could be photographed with a 14-foot concave grating. A good vacuum was found to be an essential condition, the presence of inert gases causing a faintness of the lines.

Mr. A. CAMPBELL asked if the apparatus could be used to measure magnetic fields.

Prof. R. W. Wood said there would be difficulty in determining the density of the vapour. It could be used, however, to determine the density of the vapour from a knowledge of the magnetic field.

Prof. R. W. Wood read a paper on "The Fluorescence of Sodium Vapour."

The fluorescence of sodium vapour has been investigated by allowing light of various wave-lengths to illuminate the vapour, and then studying the light emitted with a spectroscope. Approximately homogeneous light of any desired wave-length is obtained by means of a monochromatic illuminator. Some sodium is placed in a horizontal steel tube fitted with steel ends, in one of which is a circular aperture bored just above the centre. The tube is heated and the vapour rises until it reaches the hole. The light from the monochromatic illuminator passes through the hole and falls upon the vapour. The fluorescent light is then observed by means of a spectroscope either visually or by photography. It is essential that the incident light should not traverse an appreciable amount of the vapour, or the fluorescent effects are masked by those of absorption. The bright lines of the fluorescent spectrum are by no means the exact complement of the absorption spectrum. Very remarkable effects have been observed when the vapour is illuminated with a very narrow band of approximately homogeneous light, the lines in the fluorescent spectrum changing their position and appearing to dance about with the slightest change

in the wave-length of the exciting light. The motion is of course only an illusion, lines disappearing and others reappearing, like the sparks of a spintharoscope. Stokes's law is violated in a most flagrant manner, bright lines coming out on both sides of the excited region. The behaviour of the spectrum indicates that we are dealing with a number of groups of electrons, each group containing a large number of vibrators. The excitation of one of these vibrators sets the whole group going, but does not start disturbances in the other groups.

ROYAL SOCIETY OF NEW SOUTH WALES.

Annual General Meeting, May 3rd, 1905.

Prof. LIVERSIDGE, M.A., LL.D., F.R.S., Vice-President, in the Chair.

THE following gentlemen were declared duly elected Officers and Members of Council for the current year:—

President—H. A. Lenehan, F.R.A.S.

Vice-Presidents—Prof. Liversidge, LL.D., F.R.S.; Prof. Warren, M.Inst.C.E., Wh.Sc.; F. B. Guthrie, F.I.C., F.C.S.; F. H. Quaife, M.A., M.D.

Hon. Treasurer—D. Carment, F.I.A., F.F.A.

Hon. Secretaries—J. H. Maiden, F.L.S.; G. H. Knibbs, F.R.A.S.

Members of Council—S. H. Barraclough, B.E., M.M.E.; Prof. T. W. E. David, B.A., F.R.S.; H. Deane, M.A., M.Inst., C.E.; T. F. Furber, F.R.A.S.; W. M. Hamlet, F.I.C., F.C.S.; T. H. Houghton, M.Inst.C.E.; H. C. Russell, B.A., C.M.G., F.R.S.; Henry G. Smith, F.C.S.; Walter Spencer, M.D.; J. Stuart Thom.

The following letter was received from Mr. L. W. MARCKER, Consul for Denmark:—

Consulate of Denmark, Sydney, N.S.W.,
February 9th, 1905.

SIR,—The sympathy which has been shown by men of science from all parts of the world over the death of the young Danish scientist Professor Mils R. Finsen, and the numerous foreign enquiries which have been made, asking permission to take part in the movement started in Denmark to raise funds, according to the deceased's last wish, to enable the scientific institution called the Finsens Institute (to which Finsen presented the Nobel prize won by him) to continue the researches so ably begun by him, has resulted in that the original Danish Committee now has become a universal one. Sub-committees have been started in England, all over the Continent, and in America. At the request of the Danish Committee, the Consulate has received instructions from the Ministry for Foreign Affairs, Copenhagen, to place the matter before the scientific bodies in Sydney. I therefore herewith have the honour to request you kindly to be good enough to direct the attention of the members of your honoured Society to the movement. The Consular instructions are also to give any local movement which might be started all possible assistance, and I need hardly say that any information or help I can give will be given with very great pleasure.—I have, &c.,

L. W. MARCKER, Consul.

Messrs. J. H. Maiden and G. H. Knibbs,
Hon. Secretaries, Royal Society of N.S. Wales.

The following papers were read:—

"On the Occurrence of Calcium Oxalate in the Barks of the *Eucalypts*." By HENRY G. SMITH, F.C.S., Assistant Curator, Technological Museum, Sydney.

The author announces the presence, in large quantities, of calcium oxalate in the barks of several species of *Eucalyptus*. It is similar in form and appearance in all species, being well defined monoclinic crystals in stout microscopic prisms, averaging 0.0174 m.m. in length and 0.0077 m.m. in breadth, and containing one molecule of

water. A peculiarity of these is the tendency to form twins geniculate in appearance; twinned forms being pronounced in some species. From botanical and chemical evidence it is assumed that *Eucalyptus salmonophloia* of West Australia and *E. oleosa* of New South Wales belong to the same species, and that the latter tree, which most often occurs as a "Mallee," is only the degenerate stage of the former. The theory is advanced that some of the "mallees," or shrubby *Eucalypts*, have been formed through the poisoning effect of the excess of oxalic acid, acting for a long time upon species which originally grew as large trees. The tannins in those *Eucalyptus* barks containing a large amount of calcium oxalate are of very good quality, light in colour, astrigent, easily soluble, and should make leather of good quality. On evaporating the extract to dryness on the water-bath but little darkening takes place, and the product is still readily soluble. This class of *Eucalyptus* barks should, therefore, make excellent tanning extracts. From the bark residue the calcium oxalate should be profitably extracted, and the oxalic acid obtained cheaply from this practically as a by-product. The air-dried bark of *Eucalyptus salubris*, the "Gimlet" of West Australia, gives 30.5 per cent of total extract and 18.6 per cent of tannin absorbed by hide powder, and contains 16 per cent of calcium oxalate. The bark of *Eucalyptus gracilis* contains 16.66 per cent of calcium oxalate; that of *E. Behriana* 16.5 per cent; of *E. oleosa* 10.64 per cent; of *E. dumosa* 9.8 per cent; and of *E. salmonophloia* 8.34 per cent. The barks of all the *Eucalypts* tested contain calcium oxalate, although in some species in very small amount.

"Notes of Astronomical Interest, dealing with the past Eighteen Months, showing the Progress and Deductions made during that Period." By H. A. LENEHAN, F.R.A.S., Acting Government Astronomer.

OBITUARY.

PROFESSOR P. T. CLEVE.

WE regret to announce the death of Prof. P. T. Cleve, of Upsala, Sweden, which took place on June 18th last. Prof. Cleve was only sixty-five years of age, having been born in 1840. He was the leading scientific chemist in Sweden, but his fame is world-wide. His name will be chiefly known and remembered in connection with his researches on the rare earths, though his work in other departments of science, such as biology and hydrography, was of considerable importance. His first scientific paper was published in the year 1861, and since that time he has contributed a large number, on varying subjects, to different scientific societies and journals. He was an Honorary Member of the Royal Institution and Honorary Fellow of the Chemical Society.

CORRESPONDENCE.

DETERMINATION OF SUGAR BY MEANS OF FEHLING'S SOLUTION.

To the Editor of the Chemical News,

SIR,—In the CHEMICAL NEWS (vol. xci., p. 299) you publish an article upon the "Determination of Sugar by Means of Fehling's Solution," by F. P. Lavalle.

Of course the use of KOH or NaOH is well known, and reference is made to it on page 477 of the Ninth Edition of "Analyse des Harns," by Huppert and Thomas. In the *Chem. Centralblatt*, of 1879, p. 406, Hehner states that the titre of Fehling's solution depends very much upon the percentage of alkalis present, and he is perfectly

correct in asserting that an excess of alkalis should be avoided. In the case of minute quantities no accuracy of results can be obtained by the volumetric method, and it is better to employ Soxhlet's method, which gives exact results in the hands of an experienced analyst.

If, however, the volumetric method is preferred, and difficulty is found in precipitating the cuprous oxide, as, for instance, in the case of beet-sugars, a good result is often obtained by the addition of about 2 c.c. of a normal solution of chloride of calcium.

This expedient is not a new one, but perhaps not generally known.—1 am, &c.,

F. M. MRAZSEK.

29, Mincing Lane, E.C., July 8, 1905.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxi., No. 24, June 13, 1905.

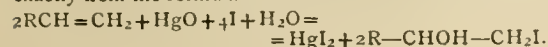
Action of Fluorine on Oxides of Nitrogen.—Henri Moissan and Paul Lebeau.—The authors make a systematic investigation of the action of fluorine on the oxygen compounds of nitrogen. After a certain number of preliminary experiments they discovered that these reactions are very complex, especially that of fluorine on nitrogen peroxide. In other cases this latter body is formed in a great number of transformations of the nitrogen compounds, and its intervention furnishes secondary reactions which complicate matters considerably.

The True Atomic Weight of Nitrogen.—G. D. Hinrichs.—The author's recent experiments, and also those performed in 1901, lead him to believe that the atomic weight of nitrogen as compared with oxygen 16 differs very slightly from 14.

A Method of Preparing Acetol and Pyruvic Acid by the Direct Oxidation of Acetone.—M. Pastureau.—By oxidising acetone by means of concentrated hydrogen peroxide, Wolfenstein obtained the superoxide $(C_3H_6O_2)_3$. Baeyer and Villiger, under slightly different conditions, obtained the superoxide $(C_3H_6O_2)_2$. By using a 2 per cent solution of hydrogen peroxide for the oxidation of the acetone the author obtains, besides the superoxide $(C_3H_6O_2)_2$, acetol and pyruvic acid. He also examines the reaction of hydrogen peroxide in acid solution on other acetones, particularly on diethylketone, methylpropylketone, and methylphenylketone, and in all cases observes the formation of acetone superoxides, ketonic alcohols, and ketonic acids.

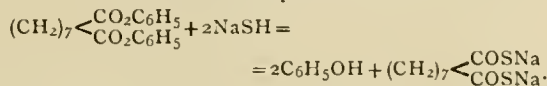
Action of Sodium on the Ethers of Monobasic Acids of the Fatty Series of Simple Function.—M. Bouveault and R. Locquin.—Sodium reacts on the ethers of the monobasic acids of the fatty series in presence of alcohol or water, in a very definite manner, and it seems probable that the reaction of the sodium and of the ether alone should be definite also, and that the bad results obtained in previous experiments are due to defective experimental conditions.

Mono-substituted Aromatic Oxides of Ethylene.—MM. Fournau and Tiffeneau.—The 1.2-mono-substituted ethylene oxides can easily be obtained from the corresponding ethylenic derivatives. The latter substances in presence of aqueous ether are acted upon by iodine, and the yellow oxide of mercury in proportions calculated exactly from the formula—



Action of Chloroacetic Ethers on the Halogen-magnesium Derivatives of Aniline.—F. Bodroux.—The action of ethyl chloroacetate on magnesium phenylamine iodide is effected in two different parts. One portion of the reagent acts on the ether-salt function, and by its own atom of chlorine produces the complex which ultimately gives iodoacetanilide. The other portion acts only through its halogen atom, and gives the ethyl iodoacetate, which persists in the mixture, and later contaminates the solid product of the operation. The result is quite different when ethyl chloroacetate and magnesium-phenylamine bromide is used. Chloroacetanilide only is formed in this case, $C_6H_5-NH-CO-CH_2Cl$.

Certain Compounds of Azelaic Acid.—A. Bouchonnet.—The author prepares thioazelaic acid from phenyl azelate. The reaction takes place as follows:—



The thioazelate of sodium thus obtained when treated with HCl gives the free acid, $(CH_2)_7 \begin{matrix} \text{COSH} \\ \text{COSH} \end{matrix}$.

Sparteine; its Action on Methyl Iodide.—Charles Moureu and Amand Valeur.—As a result of the authors' experiments on sparteine, the detail of which will be published later, they find that methyl iodide when acting upon sparteine always produces, besides the iodomethylate, which is already known, an isomer which differs chiefly in its much greater rotatory power and its extreme solubility in water.

Pyrolysis of Gum-lake.—A. Etard and E. Wallée.—The authors experiments give definite and abundant results which tend to throw some light on the constitution of resins, substances which have hitherto been somewhat neglected. There exists both an acetate of bornyl and other analogous terpenic ethers. Apparently the numerous resins seem to be the ethers of the higher acids and of the polyterpenes. Gum-lake should therefore be comparable with artificial drying compounds used as protection agents. Experimentally, this substance seems to be a non-stable oleate of a continuous series of polyterpenes. In an isolated form these drying agents are contained in a large number of vegetable species, and combined they form the base of commercial varnishes.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 3rd inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Baroness Gray was elected a Member. The Special Thanks of the Members were returned to Sir Andrew Noble, K.C.B., F.R.S., for his donation of £100 to the Fund for the Promotion of Experimental Research at Low Temperatures; and to Mr. Rollo Appleyard for his gift of a Portrait of the late Professor J. D. Everett, F.R.S., M.R.I.

American Chemical Society, June 22 to 24, 1905, Buffalo, N.Y.—The following is a list of papers read:—

"The Classification of Carbon Compounds." Marston T. Bogert.

"Some Recent Advances in Physiological Chemistry." John H. Long.

"Note on the Atomic Weight of Carbon." C. L. Parsons.

"Chemical Glassware." Percy H. Walker.

"An Apparatus for Determining the Viscosity of Liquids at Different Temperatures." F. Courtois.

"An Apparatus for Determining the Flash-point of Inflammable Liquids." F. Courtois.

- "Vapour Pressure of Sulphur at 100°." (Second paper). Hippolyte Gruener.
- "On a New Dynamic Method of Measuring Vapour Tensions of Solutions." Louis Kahlenberg.
- "Molecular Weight by Vapour Heating." H. R. Carveth and J. P. Magnusson.
- "The Hydrolysis of Ammonium Acetate and the Ionisation of Ammonium Hydroxide and Water at High Temperatures." A. A. Noyes and Yogoro Kato.
- "The Constitution of the Bronzes." W. D. Bancroft.
- "Tensile Strengths of Aluminium Zinc Alloys." W. D. Bancroft.
- "Some Alloys of Zinc." W. D. Bancroft.
- "A New Use for the Dilatometer." W. Lash Miller.
- "Equilibrium in the System $\text{BeO}:\text{C}_2\text{O}_3:\text{H}_2\text{O}$." C. L. Parsons and W. O. Robinson.
- "The Phosphates of Calcium." F. K. Cameron.
- "The Application of Physical Chemistry to Soil Studies." F. K. Cameron.
- "The Transmutation of the Elements." H. T. Barnes.
- "A Strong Sterilisable Dialysing Membrane." H. W. Hill.
- "Some Notes on Rock Decompositions." A. S. Cushman.
- "Some Observations on the Deposition of Alloys from Mixed Solutions." C. B. Jacobs.
- "Some Properties of the Metal-ammoniums." C. A. Kraus.
- "A Determination of the Coefficient of Expansion of Oxygen." Edward W. Morley and Dayton C. Miller.
- "The Isolation and Properties of some Electro-positive Radicals." C. A. Kraus.
- "The Precipitation of Colloidal Egg Albumin by Electrolytes." A. P. Matthews.
- "On the Solubility of Carbohydrates in Pyridine and the Optical Rotatory Power of the Resulting Solutions." J. G. Holty.
- "On the Dielectric Constants of certain Solvents and Solutions." J. H. Mathews.
- "Some Absorption Phenomena with Phosphates." Oswald Schreiner.
- "Dimeric Equilibria." W. D. Bancroft.
- "A Manostat." W. D. Bancroft.
- "The Constitution of Trinidad Asphalt from a Physico-chemical Point of View, and its Proximate Composition." Clifford Richardson.
- "The Action of Ethylene Dibromide on *p*-Nitrosodialkylanilines." Henry A. Torrey.
- "On the Preparation of Various Acyl Derivatives of Dimethyl 4-Amino-*o*-phthalate." M. T. Bogert and R. R. Renshaw.
- "On some Nitro- and Amino-derivatives of Fluorescein." (Preliminary Notice). M. T. Bogert and R. G. Wright.
- "Researches on Pyrimidines: On 2, 5-Diamino-6-oxypyrimidine." Treat B. Johnson.
- "On the Constitution of Phenylurazole." S. F. Acree.
- "On the Pinacone-pinacolin Re-arrangement." S. F. Acree.
- "The True Benzaldehyde-azo-benzoic Acids." Frederick J. Alway.
- "The Neutral Sulphite Method for Determining Aldehydes in Essential Oils." S. S. Sadtler.
- "The Detection and Determination of Ethyl and Methyl Alcohols in Mixtures by the Immersion Refractometer." Albert E. Leach.
- "A Comparison of Methods for the Determination of Fusel Oil." E. M. Chace and W. L. Dubois.
- "A Crucible Method for the Determination of Sulphur, Halogens, and Phosphorus in Organic Substances." S. S. Sadtler.
- "Methods for Examinations of Cellulose-nitrate and Smokeless Powders." Albert P. Sy.
- "Camphoroxalic Derivatives." J. Bishop Tingle and W. E. Hoffman, jun.
- "Rosocyanine." C. L. Jackson and Latham Clarke.
- "The Formula of Curcumine." C. L. Jackson and Latham Clarke.
- "The Reduction of 5-Nitro-4-ketodihydroquinazolines to the Corresponding Aminoquinazolines, and the Preparation of certain Derivatives of the latter." M. T. Bogert and V. J. Chambers.
- "The Synthesis of 5-Nitro-4-ketodihydroquinazolines from 6-Nitroacetantranil and Primary Amines." M. T. Bogert and H. A. Seil.
- "On Isomeric O and N Ethers Derived from 2-Alkyl-4-oxy-5-nitroquinazolines and 2-Alkyl-4-keto-5-nitrodihydroquinazolines." M. T. Bogert and H. A. Seil.
- "Some Acyl Derivatives of Homoanthranilic Nitrile and the 7-methyl-4-ketodihydroquinazolines Prepared therefrom." M. T. Bogert and A. Hoffman.
- "The Condensation of Succinylsuccinic Acid Diethyl Ester with Guanidine: A Derivative of 1, 3, 6, 8-Naphthotetrazine, a New Heterocycle." M. T. Bogert and A. W. Dox.
- "The Methoxyl Group in certain Lignocelluloses." Alvin S. Wheeler.
- "Milk Proteids and some of their Relations." L. L. Van Slyke.
- "The Physiology of Uric Acid." F. H. McCrudden.
- "Adrenaline, the Active Principle of the Suprarenal Glands." T. B. Aldrich.
- "Convenient Distillation Arrangements for Free and Albuminoid Ammonia." W. F. Mason.
- "The Purification of Water by Ozone." R. S. Weston.
- "The Purification of Water by Copper." W. H. Buhlig.
- "Colloidal Suspensions and their Relation to Problems in Water Purification." J. W. Ellms and J. F. Snell.
- "The Composition of Cooked Foods." W. D. Bigelow.
- "Artificial Digestion Experiments." Edward Gudeman.
- "Notes on Occurrence of Pentoses in Second Pressing Cider." J. A. Le Clerc and L. M. Tolman.
- "Color Tests for Cod-liver Oil." W. D. Bigelow.
- "The Presence of Hexone Bases in Bacteria." Mary F. Leach.
- "The Chemistry of Flesh." H. S. Grindley.
- "Unfermentable Matter in Glucose and Grape Sugar." A. P. Byrant.
- "The Testing of Wheat Flour for Commercial Purposes." Harry Snyder.
- "The Occurrence of Extractives in Apple-peel." H. C. Gore.
- "The Pecto-celluloses of the Apple." W. D. Bigelow and H. C. Gore.
- "A Study of the Unfermentable Reducing Matters in Hydrolytic Product of Starch." A. P. Bryant and C. S. Miner.
- "Laboratory Methods for Studying the Formation of 'Alkali.'" F. K. Cameron.
- "The Analysis of Sugar Mixtures." C. A. Browne, jun.
- "Chemical Preservatives Used in Food Products. Are they Harmful? E. W. Duckwall.
- An Address by Victor Lenher. Subject, "Tellurium."
- "Recent Work on Columbium and Tantalum." R. D. Hall.
- "On the Oxidation of Hydrazine." Arthur Wesley Browne.
- "Qualitative Analysis, its Place and Importance in Chemical Instruction." Edward Ellery.
- "The Chemical Separation of the Radio-active Types of Matter in Thorium Compounds." Herman Schlundt and Richard B. Moore.
- "On the Radio-activity of the Mineral Waters of Missouri." Hermann Schlundt and Richard B. Moore.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Ozone—I am in search of a book on Ozone, and should be extremely obliged if any correspondent could tell me of such a book. I have one by Emile Andreoli (published by H. Alabaster, 1893), which is, however, of no use to me. We are thinking of having an ozone bleaching plant, and wish to know something about ozone generally before adopting it.—OZONE.

Reclaiming Waste Rubber.—(Reply to "Waste Rubber").—Possibly the enquirer may find what he wants in my translation from the French of "Indiarubber and Gutta-percha," by T. Seeligmann, G. L. Torrilhon, and H. Falconnet (Scott, Greenwood, and Co.), i.e., if he can get a copy, as it is, I believe, almost if not quite out of print. With that book and the abridgments of patents (to be had *ad initio* for a nominal sum) I do not think any insurmountable difficulty will be encountered. Working with acids, lead-lined (i.e., lead burned) vessels will of course be necessary—and possibly these can be got as cheap and as well burnt as anywhere from Mr. Pitt, Chemical Plumber or Lead Burner, Ferry Street, Millwall, London, E. I would advise the enquirer to consult Mr. Pitt by appointment, if resident in London; or if he shows the diagrams of plant in Patent Office specifications (expired patents, of course) to any local lead burner, he will readily construct an apparatus for him. He must take care he does not get into trouble with the local authorities in regard to fumes. I do not now exactly remember whether such works come under any Local Government Board regulations or not; in any case they should. But rubber reclamation is too wide a subject to answer in a Note, but if the enquirer wants any specific information I am at his disposal through your columns.—JOHN GEORGE MCINTOSH, 9, Parsonage Street, Cubitt Town, E.



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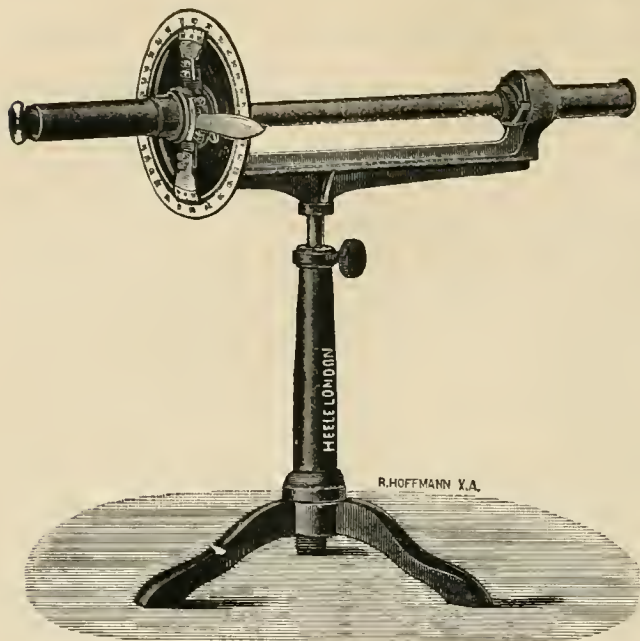
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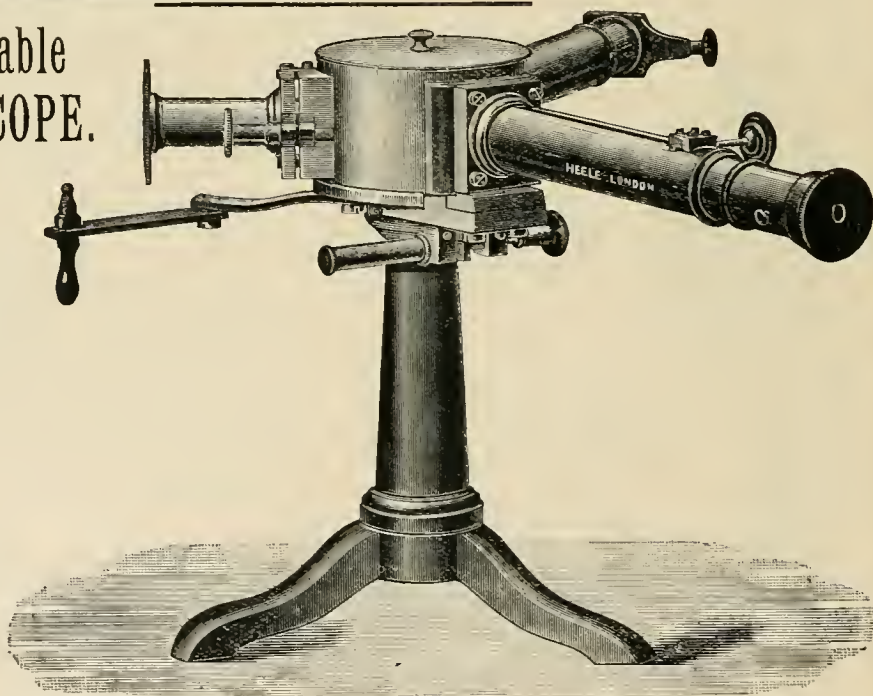
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VOL. XCIII., No. 2382.

ON THE PHOSPHORESCENT SPECTRA OF Sδ AND EUROPIUM.*

By Sir WILLIAM CROOKES, D.Sc., F.R.S.

THE recent examination of a pure specimen of europium prepared by M. Urbain has brought to light some interesting facts connected with its phosphorescent spectrum when the sulphate is subjected to cathode radiations in a radiant matter tube.

In Demarcay's paper announcing the discovery of europium (*Comptes Rendus*, cxxxi., p. 1484; *CHEMICAL NEWS*, lxxxiv., p. 1), he referred to the phosphorescent spectrum of the new earth in the following terms:—

"In 1885 Sir William Crookes, during his beautiful researches on electric phosphorescence *in vacuo*, noticed a band which he attributed to samarium, and which, by reason of its disappearance in the presence of lime and from certain other peculiarities, he called the 'anomalous line.' Later he distinguished this, together with a large number of other bands, as belonging each to a special meta-element. The hypothetical meta-element corresponding to the anomalous line he called Sδ. M. Lecoq de Boisbaudran, in the course of his important researches on phosphorescence, confirmed the above statements with regard to this anomalous line. In 1892 M. de Boisbaudran described a spectrum consisting of three brilliant blue lines discovered in the spark spectrum of samarium. He concluded that they corresponded to a particular element, Zε. About the same time he also drew attention to a particular band in the reversal spectrum of samarium, which apparently corresponded to the anomalous line. M. de Boisbaudran, without forming very precise conclusions, inclined to the idea that this line was due to a particular element, Zζ. In 1896 I discovered the presence of an element intermediate between gadolinium and samarium. In 1900 I showed that this new element was identical with de Boisbaudran's Zε, and that Crookes's anomalous band was due to the same substance, as well as the reversal line Zζ. . . . Since that period, by a long series of fractionations with magnesium nitrate, I have been able to accumulate a considerable quantity of this element. The apparently contradictory results of Crookes and de Boisbaudran are due, I think, to the very small proportions of Z—Zε contained in their material. I propose the name Europium for the new element, with symbol Eu, and atomic weight 151 (approx.)."

Immediately on the publication of Demarcay's paper I gave reasons why my earth giving the very sharp red phosphorescent line (which I had called "the anomalous line"), was not the same as either de Boisbaudran's or Demarcay's earth. I said (*CHEMICAL NEWS*, vol. lxxxiv., p. 2, July 5, 1901):—

"It is necessary for me to make one or two corrections to the paper of M. Demarcay.

"I have never admitted that the body called by M. de Boisbaudran Zε is the same body which gives my 'anomalous line.' Indeed, I have good reason to think they are quite different. The line given by M. de Boisbaudran's Zε is broad and indistinct at the edges, while the 'anomalous line' is absolutely sharp and narrow, like a gas-line. Also their refrangibilities are not identical. The same remarks will apply to the body described by M. Demarcay in his 1900 paper."

The first record of the observation of the so-called anomalous line is in my paper "On Radiant Matter Spectroscopy—Part II., Samarium," read before the Royal Society, June 18, 1885 (*Phil. Trans.*, Part II., 1885), which contains an account of the conditions under which this line is obtained and my reasons for supposing it to be indicative of an elementary substance. In Paragraph 146, I said:—

"It was interesting to ascertain what spectrum a mixture of samarium and yttrium would give. . . . I next tried a mixture of samaria 80, and yttria 20. The spectrum was identical with the one last observed, with one striking difference—the λ-2 2693 line now shines out with great brilliancy of a fine orange-red colour, as sharp as a gas line, and so unlike the bands usually met with in the spectra of phosphorescent earths as to suggest the explanation that some other spectrum-forming body was present in the mixture."

Again, in the same paper, Paragraph 165, I wrote:—

"The Anomalous Line λ-2 2693.—On several occasions I have spoken of an orange line, λ-2 2693, which by its brilliancy and sharpness is a prominent object in most of the samarium-yttrium spectra. With samaria sulphate it is exceedingly faint. With samaria containing 5 per cent of yttria it is very little brighter; . . . and with a mixture of 80 parts samaria and 20 parts yttria it is at its maximum intensity."

The next year I returned to the subject, and in a paper "On some New Elements in Gadolinite and Samarskite, Detected Spectroscopically (*Proc. Roy. Soc.*, June 9, 1886, vol. xl., p. 502), I said that I had since further investigated the occurrence of line λ 6094, "the anomalous line," with the bringing to light of some important new facts. I found that the body giving rise to the line closely followed samarium in my fractionations, and that the presence of yttria was not necessary to bring it out, the yttria acting only by deadening the brightness of the other red, green, and orange bands of samaria, while it had little or no action on the anomalous line. Again, I found that the addition of a little lime entirely suppressed line λ 6094, while it brought out the samarium lines with increased vigour. I further found that in samaria prepared from different minerals the line varied greatly in intensity. The earth from samarskite showing it strongly, while samaria from gadolinite showed no trace of line λ 6094. "It follows, therefore, that the body whose phosphorescent spectrum gives line λ 6094 occurs in samarskite but not in gadolinite; thus it cannot be due to samarium, yttrium, or a mixture of these two elements. The only other probable alternative is that the source of this line is a new element."

I said:—"A hitherto unrecognised band in the spectra by absorption or phosphorescence is not of itself definite proof of a new element, but if it is supported by chemical facts, such as I have brought forward, there is sufficient *prima facie* evidence that a new element is present. Until, however, the new earths are separated in sufficient purity to enable their atomic weights to be approximately determined, and their chemical and physical properties observed, I think it is more prudent to regard them as elements on probation." I therefore named the new body Sδ, the S recalling the source, samarskite.

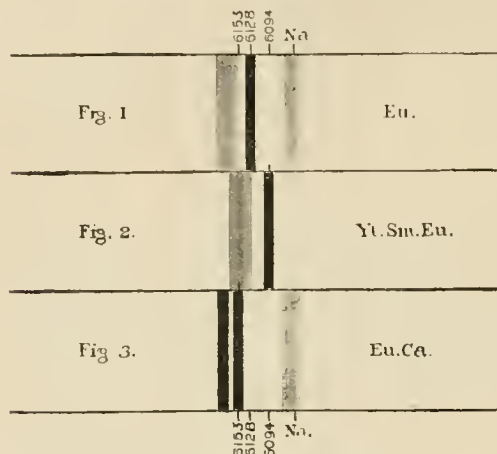
In 1887, I again recurred to the subject of line λ 6094, and in a paper communicated to the Royal Society on February 10, 1887 (*Proc. Roy. Soc.*, vol. xlii., p. 112), I gave the result of an extended search for the earth which gave rise to it, or Sδ. I said that Sδ "is not present in the rare earths from gadolinite, xenotime, monazite, hielmite, euxenite, and arhenite; it is present in small quantity in cerite, and somewhat more plentifully in samarskite. . . . In samarskite yttrium it concentrates at a definite part of the fractionation. A little calcium entirely suppresses the orange line, while samarium or yttrium seem to intensify it."

Owing to want of material and pressure of other occupations, the subject was put aside until recently, when an examination of the phosphorescent spectrum of Urbain's

* A Paper read before the Royal Society, June 8, 1905.

pure europium, in the form of ignited sulphate, led me to take up the matter once more.

Europium sulphate phosphoresces red, as described by Demarçay. A photograph showed a complete absence of phosphorescence bands between λ 4800 and λ 2536. The visible spectrum consists almost exclusively of two red lines, the most refrangible being nebulous and faint, the other sharper and very bright (Fig. 1), and a faint nebosity in the position of the sodium line.



The strong phosphorescent line, which Demarçay thinks is identical with my $S\delta$, is shown by europia and gadolinia; indeed, it is stronger in gadolinia than in europia. Careful measurement shows it is not coincident with the old anomalous line, the wave-length of the europia line being λ 6128 and that of $S\delta$ λ 6094.

Experiments were made in connection with the appearance of $S\delta$ and the identity or non-identity of it with the similar looking line in Urbain's earths. Some good yttria was mixed with pure samaria in the proportion originally found to give the $S\delta$ line most brilliantly, but the phosphorescing sulphate failed to show any trace of it. To this mixture was now added a little europia, and the $S\delta$ line was developed brilliantly, and occupied its normal position at λ 6094 (Fig. 2), in a different position to the line seen when the europia is not contaminated with Yt and Sm. This result was so unusual that both tubes, one containing europium sulphate, and the other Eu, Yt, and Sm sulphate, were arranged so that their two spectra overlapped, when the difference in position was very marked.

It having been found that the addition of lime caused the anomalous line to disappear, it was decided to add lime to pure europia to ascertain its effect. It did not suppress the Eu line, but caused it to shift towards the red to λ 6153, still further away from the position it occupied in mixtures of Yt, Sm, and Eu; and its less refrangible companion, shown faint in Figs. 1 and 2, increased to almost equal intensity (Fig. 3).

Sparteïn. Stereoisomerism of the Two Iodomethylates.—Charles Moureu and Amand Valeur.—The two isomeric iodohydrates of sparteïn iodomethylate can be decomposed quantitatively, under the influence of heat, into methyl iodide and sparteïn iodohydrate, the action being the same in the two cases. The action of methyl iodide on sparteïn iodohydrate gives rise to two iodomethylates (united with hydriodic acid). In the two isomeric iodomethylates the methyl iodide is fixed on to the same nitrogen atom. It follows from these facts that the isomerism of the two bodies can only be due to a different disposition in space of the radicals round the same atom of nitrogen. In other words, it is of a stereochemical order.—*Comptes Rendus*, cxl., No. 25.

THORIANITE, A NEW MINERAL FROM CEYLON.*

By WYNNDHAM R. DUNSTAN, M.A., LL.D., F.R.S.,

and

G. S. BLAKE, A.R.S.M.,

Assistant in the Scientific and Technical Department of the Imperial Institute.

(Concluded from p. 15).

Composition of Thorianite.

THE methods used in determining the composition of thorianite are founded on those suggested by Glaser (*Zeit. Anal. Chem.*, 1897, vol. xxxvi., p. 213), Meyer and Markwald (*Ber.*, 1900, vol. xxxiii., p. 3003), Fresenius and Hintz (*Zeit. Anal. Chem.*, vol. xxxv., p. 343), and Benz (*Zeit. Ang. Chem.*, 1902, p. 297).

The results are shown in the accompanying table, which includes the data obtained from three separate specimens, numbered I., II., and III.

Analyses of Thorianite.

	I. Per cent.	II. Per cent.	III. Per cent.
Soluble in nitric acid—			
Thorium dioxide	72.24	76.22	78.86
Uranium dioxide	11.19	12.33	6.03
Uranium trioxide	—	—	9.07
Cerium dioxide	6.39	—	—
Lanthanum and didymium oxides	0.51	8.04	1.02
Yttrium oxide	—	—	—
Lead oxide	2.25	2.87	2.59
Ferric oxide	1.92	0.35	0.46
Calcium oxide	—	—	1.13
Helium	—	—	0.39*
Titanium dioxide	—	—	—
Phosphoric oxide	—	—	Trace
Insoluble in nitric acid—			
Zirconium oxide	3.68	—	0.20
Silica	1.34	0.12	—
Residue from fusion with potassium-hydrogen sulphate	0.41	—	—

* If the whole of the gas is calculated as helium.

In the estimation of the metals, 2 grms. of the finely powdered mineral were dissolved in about 15 c.c. of nitric acid of specific gravity 1.4, and after decomposition was complete the solution was diluted and filtered. The insoluble residues in specimens II. and III. were very small, and were treated with hydrofluoric acid to estimate silica. In I. the residue chiefly consisted of zircon which was fused with potassium hydrogen sulphate to extract zirconia, and the residue treated as before with hydrofluoric acid to estimate silica. Except for this associated zircon, no zirconia was found in the mineral.

The acid filtrate from the insoluble residue was diluted to about 300 c.c. and 5 c.c. of hydrochloric acid added. Hydrogen sulphide was then passed through the liquid to precipitate lead which was finally weighed as sulphate. The filtrate was boiled to remove hydrogen sulphide, and oxidation of the last traces of this substance effected with bromine water. To the hot acid solution, amounting to about 350 c.c., excess of ammonium oxalate was added, and the precipitate of oxalates of thorium and cerium, &c., allowed to settle overnight and then filtered. The filtrate was evaporated to dryness and treated with nitric acid to destroy oxalic acid, and diluted with water. The calcium and magnesium were separated from other metals by precipitating the latter with ammonia and ammonium chloride. This precipitate was dissolved in hydrochloric acid, excess of acid neutralised, and the solution diluted to 500 c.c. A few drops of solution of sodium sulphite were added, and the liquid boiled to precipitate any titanous acid. No

* A Paper read before the Royal Society, May 18, 1905.

titanium was, however, present. The liquid was evaporated, and the iron oxidised with a few drops of nitric acid. The liquid was neutralised with a few drops of ammonia, and finally excess of ammonium carbonate added. The carbonates first precipitated were re-dissolved on further addition of the reagents, showing the absence of alumina. The iron was separated as sulphide. The filtrate was boiled, acidified with hydrochloric acid, and again boiled to remove all the carbon dioxide. The uranium in solution was precipitated with ammonia, and finally weighed as uranosouranic oxide, U_3O_8 .

The precipitate containing the oxalates of thorium and cerium, &c., was dried, and the oxalates were then decomposed by nitric acid, and the metals obtained in solution as nitrates. After diluting to 250 c.c., sodium thiosulphate was added to the slightly acid boiling liquid till no further precipitate of thorium salt was obtained. The liquid was boiled for a short time, the precipitate filtered off and dissolved in hydrochloric acid, and the operation twice repeated to completely separate the cerium. To the united filtrates ammonia was added, and the precipitate of hydroxides of the cerium, &c., containing a little thorium and any yttrium present, was dissolved in hydrochloric acid, and the trace of thorium precipitated as above described from a small bulk of liquid. The thorium precipitates were dissolved in hydrochloric acid, and the thorium re-precipitated as hydroxide and finally weighed as the dioxide ThO_2 . The filtrate from precipitation of the cerium earths with ammonia contains lime if such were present in the original mineral. This was separated as oxalate and weighed as oxide.

Determinations of the equivalent of thorium made with the precipitated dioxide obtained in the course of the analysis of the third specimen (see p. 26) by conversion into the sulphate gave 57.25, corresponding with an atomic weight of 229. The accepted atomic weight of thorium, relative to hydrogen taken as 1, is 230.8.

The solution from which thorium had been thus removed, containing cerium and the associated earths, including any yttrium, was treated with ammonia; the precipitate dissolved in dilute sulphuric acid, and the solution, after neutralisation, saturated with potassium sulphate. No yttrium was found in the filtrate by dilution and addition of ammonia.

The double sulphates of potassium with cerium, and of the associated metals lanthanum and didymium, were warmed with ammonia solution, by which means the earths were obtained as hydroxides. These were dissolved in hydrochloric acid and re-precipitated by potash solution. The hydroxides were washed by decantation, a little potash solution added, and chlorine gas passed until the liquid was saturated. The lemon-coloured hydrated ceric oxide was filtered off, re-dissolved, and re-precipitated as hydroxide, and the cerium weighed as the dioxide CeO_2 . The filtrate containing lanthanum and so-called didymium was acidified with hydrochloric acid, boiled to remove chlorine, and the earths precipitated with ammonia and weighed as the oxides.

The uranous oxide (UO_2) was separately estimated by Hillebrand's method as follows:—One or 2 grms. of finely powdered mineral were introduced into a stout tube together with 20 to 30 c.c. of dilute sulphuric acid, consisting of one part of acid to five parts of water. The air was then displaced by carbon dioxide, the tube sealed off, and then heated to 180° C. for several hours till decomposition was complete. The solution obtained was diluted with recently boiled water, and the uranous sulphate titrated with potassium permanganate.

The method adopted for the determination of helium and associated gases consisted in decomposing the mineral by means of dilute sulphuric acid consisting of one part of acid to five parts of water (Hillebrand, *loc. cit.*). Ten grms. of the powdered mineral were used, and the gas collected in a gas burette over mercury with the usual precautions. The mixture was heated at 100°. Decomposition at this temperature was almost complete in one day, but the

experiment was allowed to continue for two days to ensure the liberation of all the gas.

The gas collected amounted to 105 c.c. at standard temperature and pressure, which corresponds to 10.5 c.c. of gas, chiefly helium, from 1 gm. of thorianite.

Of the three specimens of thorianite analysed the first was too small to admit of any treatment to separate associated minerals, and proved to contain associated zircon. Specimens II. and III. were separated as far as possible from extraneous minerals, and represent a nearer approach to the single mineral. The highest amount of thorium yet found is nearly 79 per cent, which shows that thorianite is the richest mineral in thorium at present known.

Constitution of Thorianite.

From the analytical results, it will be seen that the constituents other than thorium show, as was to be expected in a mineral of this character, some variation. In Nos. I. and II. cerium dioxide occurs up to the extent of 8 per cent, while in No. III. it becomes almost insignificant. The uranium appears to occur in the condition of both uranous and uranic oxides. It is, however, intended to further investigate this question, since the presence of uranic oxide on the surface of some specimens would indicate that the mineral may have suffered considerable superficial oxidation, and that crystals may be found containing a much smaller proportion of uranic oxide. Of the other oxides present, zirconia in the insoluble residue may be safely classed as an impurity arising from zircons which are invariably found with thorianite, sometimes included within the crystalline thorianite. Silica and ferric oxide may be neglected as contaminations. Leaving out of consideration for the present the oxides of lead and calcium (not a constant constituent) the mineral consists of a large amount of oxide of thorium and a small amount of oxides of uranium, with a smaller and variable amount of cerium oxide, the precise significance of which is at present doubtful.

In the original condition the uranium may have existed entirely as dioxide. There can be little doubt that the dioxides of thorium and uranium, as well as certain of the salts of these metals, are isomorphous. In nature these oxides have not been found in a pure crystalline state, but crystals of each have been obtained artificially. Crystalline thorium was obtained by Troost and Anouard (*Comptes Rendus*, 1886, vol. cii., p. 1422), whilst studying the relation between the double phosphate of potassium and thorium and that of potassium and zirconium. The phosphates were first obtained by adding to fused potassium orthophosphate, thorium phosphate, or anhydrous thorium chloride. On raising the double phosphate to such a temperature that both alkali and phosphoric acid were volatilised, thorium was obtained in crystals belonging to the cubic system; the cuboctahedron and rhombic dodecahedron being the forms observed (*loc. cit.*). Again, uranium oxide was first obtained in an octahedral form by Wohler by heating a mixture of uranium oxychloride with sodium chloride and ammonium chloride (*Liebig's Annalen*, 1842, vol. xli., p. 345). Later, Hillebrand repeated the experiment, and obtained practically pure uranium dioxide in black octahedral crystals of a specific gravity of about 11 (*Zeit. f. Anorg. Chemie*, 1893, vol. iii., p. 243).

The hydrate of thorium sulphate $Th(SO_4)_2 \cdot 9H_2O$ is also, according to Rammelsberg (*Berl. Acad. Ber.*, 1886, p. 603), monoclinic in crystalline form and isomorphous with the corresponding hydrate of the uranium salt $U(SO_4)_2 \cdot 9H_2O$.

Our analyses of different specimens of thorianite are hardly sufficiently numerous to enable us to conclude that the oxides of thorium and uranium bear a definite relation to one another in the mineral. It seems probable that the mineral belongs to the class of substances known as isomorphous mixtures, of which the simple form would be represented by the formula NO_2 , where N represents a tetravalent element the dioxide of which crystallises in the isometric system the extremes of which would be UO_2 and ThO_2 .

Thorianite is evidently closely related to uraninite (pitchblende) in constitution. The crystalline form of the two minerals is the same and the constituents of both are similar. Hillebrand's analysis of the Branchville varieties of uraninite, which were stated to be nearly unoxidised, furnished 72.25 per cent of uranium dioxide and only 13.27 of uranium trioxide (*Amer. Jour. Sci.*, 1890, vol. xl., p. 384). Uranium dioxide very readily oxidises on exposure to air, and it was only by completely excluding the air that Hillebrand succeeded in obtaining the pure oxide artificially. It is therefore certain that the natural varieties of the oxide so far examined must have suffered alteration and oxidation, and that originally their principal constituent was uranium dioxide. Most of the massive varieties of uraninite are very impure, and this may account in a large measure for the presence of many oxides in this mineral which appear to have very little in common with the principal constituents. Lead oxide is apparently generally present in thorianite. It occurs in small amount and may be combined as uranate. In the case of thorianite the crystallographic examination has shown that the mineral has crystallised with difficulty, and that it is more or less contaminated with those minerals which crystallised at the same time, as well as with impurities contained in the magma from which crystallisation occurred.

As far as the present investigation has gone it appears probable that thorianite is isomorphous with uraninite, and that in the thorianite of Ceylon some of the thorium is replaced by the corresponding uranium oxide. The evidence, however, is not sufficient to show whether this is a case of isomorphous mixture, as seems probable, or of true chemical replacement.

It is obvious that the mineral is one of exceptional interest, and that it presents many problems for investigation, among them being the question of the possible occurrence of small quantities of hitherto little known or unknown elements.* The material furnishes a satisfactory source of pure thorium, a fact which is of commercial importance as well as of scientific interest.

We have shown that thorianite is chiefly composed of thorium, as at present understood. Baskerville believes that he has obtained evidence that the substance at present known as thorium is composed of more than one element, and that he has separated thorium into three oxides differing in density, and one of which is little, if at all, radio-active. These conclusions have, however, been called in question by Meyer and Gompertz (*Ber.*, 1905, vol. iii., p. 187), who assert that thorium shows no evidence of being other than a single substance.

Determination of the rate of decay of the radio activity of thorianite made in Lord Blythwood's laboratory by Mr. H. S. Allen have shown that this property of the mineral is probably consistent with the thorium, uranium, and small amount of radium present.

The radio-activity of the mineral was measured in a parallel plate apparatus, using sufficient material to entirely cover the lower plate. The observed rate of leak under these conditions was 6900 divisions per minute, equivalent to a current through the apparatus of approximately 5.5×10^{-11} amperes. Thorianite is, therefore, somewhat active than some of the specimens of pitchblende examined by Madame Curie, whose results with this mineral are as follows:—

Pitchblende from Johanngeorgenstadt	8.3×10^{-11} amperes
" " Joachimstahl	7.0×10^{-11} "
" " Pzibran	6.5×10^{-11} "
" " Cornwall	1.6×10^{-11} "

A series of measurements of the rate of decay of activity of the emanation from thorianite have been made;

* Since this was written Hahn, in a communication to the Royal Society (*Roy. Soc. Proc.*, 1905) has announced the existence in thorianite of a small quantity of a new element, which produces the "thorium emanation." This was separated from the 6 cwt. of the mineral referred to earlier in this paper. It must not be overlooked that the consignment, though apparently worked up as a whole, was doubtless a mixture containing several other minerals than thorianite.

16.5 gms. of the mineral were heated in a hard glass tube, and the emanation, previously dried over phosphorus pentoxide, collected in the testing vessel. It was set aside for 6 hours in order to allow the thorium emanation to decay, and then measurements of the activity were made daily.

The results showed that during the first four days the rate of decay was greater than that observed by Rutherford for radium emanation, but that after this period the rate of decay of activity became identical with that of radium emanation. It is probable that the greater rate of decay during the first four days was due to the presence of thorium "excited activity" which, according to Rutherford, decays to half value in the course of 11 hours, whereas the radium emanation falls to half value only in about 3.7 days.

These results clearly indicate the presence of radium emanation in the "total emanation" from thorianite, and that consequently this mineral must contain radium.

Commercial Value of Thorianite.

Owing to the increasing employment of thorium for the manufacture of incandescent gas mantles, the demand for minerals containing thorium has largely increased. The demand is chiefly met from the deposits of sand containing a small percentage of monazite (phosphate of the cerium metals and thorium) which occur in Brazil and in North Carolina. Owing to the foreign control of these sands, British manufacturers have experienced difficulty in manufacturing thorium compounds. Thorianite is, we believe, the first deposit of a thorium mineral to be discovered on British territory. Consignments of thorianite from Ceylon, containing about 70 per cent of thorium, have been recently sold in this country at the rate of £1500 per ton.

For the manufacture of thorium compounds thorianite possesses the advantage, not shared by any known thorium mineral, of containing uncombined thorium, soluble in nitric acid with formation of thorium nitrate.

THE DECAY CONSTANT OF RADIIUM EMANATION.

By O. SACKUR.

THE decay constant of radium emanation has been found by P. Curie (*Comptes Rendus*, 1903, cxxxv., 857) to be 2.02×10^{-6} , and by Rutherford and Soddy (*Phil. Mag.*, 1903, [6], v., 441) to be 2.16×10^{-6} . Hence the time in which the activity of the emanation sinks to half its value is calculated to 3.98 days and 3.71 days respectively. As the determination of the rate of decomposition of the emanation is the most convenient and accurate way of identifying and analytically proving the presence of radio-active elements, it seemed desirable to establish the value of the decay constant of radium emanation as exactly as possible, and to explain the above mentioned difference. This difference might possibly be caused by the difference in the methods employed by the investigators. Thus Curie determined the loss of activity of a closed tube filled with the emanation, its conductivity being thus caused by the emanation itself and by the induced activity formed upon the walls, while Rutherford and Soddy, on the other hand, in each experiment filled the measuring tube with the emanation which was stored in a gasometer, and determined the conductivity directly after it had been blown in, thus before an appreciable amount of induced activity had been formed. Both methods lead to the same values of the decay constant if in each moment the induced activity is proportional to the strength of the emanation, which is generally assumed to be the case. If i denotes the measured activity, L the part due to the emanation, and i' that due to the induced activity, then—

$$\begin{aligned} \text{According to Rutherford and Soddy} \quad & i = i' \\ \text{According to Curie} \quad & i = i' + i'' \end{aligned}$$

By the exponential law $i' = i_0' e^{-\lambda t}$, and, moreover, $i'' = k i' = k i_0' e^{-\lambda t}$; thus $i = i_0' (1 + k) e^{-\lambda t} = i_0'' e^{-\lambda t}$.

As Curie found the exponential law was confirmed in his experiments the assumption of the proportionality of emanation and induced activity is proved, and the value obtained by him is the decay constant of radium emanation.

To determine λ more accurately I employed the experimental arrangement described by Rutherford and Soddy. Some bubbles of radium emanation, which had formed in a solution of 1 m.grm. of radium bromide in 1 c.c. of water, were mixed with about 10 litres of air, thus diluted ten million times, and kept in a gasometer over water. After definite intervals of time (one or more days), a measured volume was drawn off by a gas pipette, dried by a phosphorus pentoxide tube, and introduced into the measuring tube, the conductivity of which was measured first at intervals of a few minutes and then at intervals of quarters of an hour. The current was supplied by an accumulator battery of 200 cells, and a Thomson's electrometer served as the measuring instrument. In the first fifteen minutes the conductivity increases very rapidly in consequence of the induced activity resulting on the walls, and then more slowly till it reaches a constant value after about two hours; the emanation was then expelled.

Table I. shows this increase of conductivity after the measuring tube has been filled. As the gasometer containing the emanation was not in the same room as the electrometer, the first measurement could not be taken sooner than two minutes after filling. The numbers denote the scale divisions which the image of the electrometer needle travels over in ten seconds.

TABLE I.*

Time after filling.	Conductivity.
Mins.	
2	266
5	282
8	305
11	313
15	317
41	352
71	385
101	403
146	410
160	403

If the corresponding curves are drawn, we can read off with sufficient accuracy what value the conductivity would have after, for example, fifteen, thirty, and sixty minutes. The comparison of these numbers on different days after filling the gasometer gives the decay constant of radium emanation.

Table II. gives these values and the corresponding common logarithms.

TABLE II.

Age of the emanation.	Conductivity.			Logarithms.		
	I.	II.	III.	I.	II.	III.
	15 mins.	30 mins.	60 mins.	t.	II.	III.
Hours.						
0	362	379	404	2.558	2.578	2.606
51	253	266	286	2.402	2.422	2.455
73	200	212	233	2.301	2.325	2.367
146	123	129.5	136	2.085	2.112	2.133
170	102	106	111	2.008	2.025	2.043
214	75.6	78.0	83.1	1.878	1.892	1.919

As the graphic representation shows, the logarithm of the conductivity decreases in all three series with the time, and thus is itself an exponential function of the time. $i = i_0 10^{-\lambda' t}$, the numerical value of λ' (in the common system) if the time is reckoned in hours, from Series I. = 0.00324, from Series II. = 0.00324, and from Series III. = 0.00321. This agreement is a further proof of the

proportionality of the emanation and the induced activity produced by it.

A second series of experiments in which the readings were taken every half hour after filling the measuring tube is shown in Table III.

TABLE III.

Age of emanation.	Conductivity.	Logarithm.
0	345	2.537
123.5	143	2.155
168	96.2	1.983
196	75.2	1.875
241	57.5	1.739
316	31.4	1.457
363	19.5	1.284
484.5	7.7	0.886

Table III. gives the value 0.00330 for the constant λ' in the common system. The mean of all four values is thus 0.00325, and in the natural system 0.0075. The decay constant λ of radium emanation thus amounts to $0.0075 = 2.08 \times 10^{-6}$, if the time is reckoned in seconds.

Consequently, the activity of the emanation decreases to half its value in 92.6 hours = 3.86 days. This number is the mean of those given by Rutherford and Soddy, and by Curie.—*Berichte*, 1905, xxxviii., 1753.

SEPARATION OF PLATINUM AND IRIDIUM.

By L. QUENNESSEN.

THE method I now describe gives a rapid process of separation of platinum and iridium; further, it is applicable to the treatment of the residues of wires, plates, and laboratory utensils with the view to obtaining pure reagents. I was led to this new method of separation in order to obviate the difficulties presented by certain processes and the inaccuracy of others. I will first recapitulate all the methods previously described, only briefly alluding to the parts concerning platinum and iridium, and will make in each case whatever criticism I consider necessary. It must be understood that there is no question of estimating these metals in their ores, but only of their alloys.

Berzelius was the first to suggest an analytical process for estimating the metals contained in the platinum group, with the exception of ruthenium, which only became known by the later investigations of Claus, and especially in more recent times by the remarkable researches of Joly.

After treating platinum and iridium with aqua regia, and removing the nitrous fumes with hydrochloric acid, Berzelius converted them into the chlor-platinate and chlor-iridate of potassium. These salts were dried, mixed with twice their weight of alkaline carbonate, the mixture placed in a crucible and raised to a high temperature, which finally yielded metallic platinum and the sesquioxide of iridium, insoluble in acids and aqua regia; after washing the ignited residue to remove the alkaline chlorides, a mixture of hydrochloric and nitric acid, diluted with an equal volume of water, was added, which dissolved only the platinum, the latter being precipitated from the solution by ammonium chloride.

The objection to this process is, in the first place, the large amount of alkaline salts used, and especially the difficulty experienced in removing them from the sesquioxide of iridium, which, as I shall presently show, is soluble in dilute acid.

Claus, in 1854, advised the use of sulphurous acid in order to reduce IrCl_4 to Ir_2Cl_6 , which, converted into the double chloride of ammonium or potassium, is soluble in an excess of these chlorides in solution. The drawback to this method is that, if the action of the sulphurous acid is too prolonged, it gives rise to the formation of the double sulphite, the treatment of which is laborious.

* A complicated equation for this increase of the induced activity has been worked out by Curie and Dancie (*Comptes Rendus*, cxxxviii., 683) and confirmed by Duaoe (*ibid.*, cxi., 581).

Muckle and Wöhler, in 1857, treated the chloro-platinate and chloro-iridate of potassium with potassium cyanide; they themselves knew that this method was not quantitative.

In 1867, Voldemar de Schneider treated a solution of platinum and iridium in hydrochloric acid with soda; he thus reduced the iridium chloride into sesquichloride, then into sesquioxide. On adding hydrochloric acid, he obtained in solution iridium sesquichloride and sodium chloro-platinate, and he precipitated the latter with ammonium chloride. But as the reduction by soda is never complete, the remaining iridium is re-formed by the addition of HCl into the tetrachloride, which separates with the platinum as the insoluble double salt. Further, the precipitation of the platinum is never total when the double sodium chloride is treated with ammonium chloride.

It was in 1877 that Sainte-Claire Deville and Stas, by their masterly work, effected a radical separation of platinum and iridium. This classic process consists in treating the two metals with molten lead; the platinum gives an alloy, Pt.Pb, soluble in dilute aqua regia, whilst the iridium forms no alloy with lead, and remains absolutely insoluble. This analytical method is, unfortunately, a slow one, and necessitates certain manipulations employed with success by Messrs. Matthey (London), which were communicated to Sainte-Claire Deville and Stas, but which the latter did not feel at liberty to publish.

Hereaus, in 1873, treated the alloy with aqua regia under pressure, evaporated the acid, and heated the residue to between 150° and 200° in order to transform the iridic chloride into the lower chloride.

This treatment under pressure was suggested as practically possible by Sainte-Claire Deville and Debray in 1861, by using commercial products then in use for attacking the ore. A. Quennessen had shown them that these platinum products, rich in iridium, possessed the property of insolubility when previously heated with aqua regia, which removed the greater part of the platinum of the surface alloy, a porous metallic layer being thus formed, very rich in iridium.

Iridium tetrachloride, under the conditions above mentioned, cannot be converted into sesquichloride.

Next followed the work of Seubert in 1881; after his determination of the atomic weight of platinum he employed the method given by V. de Schneider, and recognised the fact that this was nothing more than a means of purification.

Mylius and Detz, in 1899, suggested the use of hydroxylamine hydrochloride for the reduction of iridium chloride, the platinum being precipitated by ammonium chloride. IrCl_3 , treated in the warm by this reducing agent, acquires a yellowish colour, not the green tint belonging to Ir_2Cl_6 ; as for the platinum chloride, its yellow colour becomes slightly reddish, and it is no longer precipitated by ammonium chloride. These authors, who introduced a variation of the method of Deville and Stas, have thus contributed to no improvement.

The last process is due to Leidié, in 1901. His publication is too recent for it to be necessary that I should review the mode of operation. It is the only process suitable to apply for the separation of the common metals of the platinum group—in order to effect a purification of the latter; but the method is not quantitative for platinum, iridium, nor rhodium. For it frequently happens that when the solution of the double nitrites is saturated with alkaline chloride, platinum is precipitated with rhodium and iridium, by the action of ammonium chloride, as the double nitrite of ammonia, and on treating the mixture of the salts of these metals with aqua regia, part of the platinum is precipitated and transformed into the insoluble nitrosyl salt, which will be described when the researches upon this salt are finished. I propose to operate in the following manner:—

The alloy to be analysed is treated with aqua regia of known composition: nitric acid ($D = 1.32$), 1 volume; hydrochloric acid ($D = 1.18$), 2 volumes; when solution is complete the

excess of nitric acid is first carefully removed, finally raising it to 120° in the oven, to eliminate the remainder of free acid; then water is added, and the metals precipitated from solution by magnesium. The precipitate is dried and ignited, then heated to dull redness in a current of hydrogen. After cooling the excess of magnesium is removed by sulphuric acid (diluted to one-tenth), and the residue treated with aqua regia, diluted with three times its volume of water; the platinum only dissolves, is converted into the double ammonium chloride, and ignited at the lowest temperature possible in order to avoid a sensible loss of metal in the form of PtCl_2 ; the use of a reducing agent is recommended, oxalic acid or glucose. The most simple means, in my opinion, consists in placing upside down in the crucible the filter containing the dried precipitate, and heating the covered crucible in the furnace; the charred paper then acts as a reducing agent, and its combustion is completed, when the operation is over, in contact with air.

In this operation I discovered that the iridium precipitated by magnesium, while still moist, is soluble in dilute sulphuric acid and in acetic acid; that it preserves this property if dried at 100°, and even at a low red heat; it is therefore probably an oxide which acquires a blue tint after drying at 100°, and whose solutions are differently coloured according to the temperature to which it has been raised.

Moist or dried at 100°, it imparts a yellow colour to dilute sulphuric acid, gradually changing to violet, and a green colour to acetic acid; it is violet with sulphuric acid if heated in air to 440°, and finally blue if raised to 800°.

I am keeping to study last of all these oxides which present such strange characteristics, contradicting what was already known of the oxides of iridium.

THORIA, THE ESTIMATION AND SEPARATION OF FROM THE YTTRIUM-CERIUM GROUP OF OXIDES.

By W. B. GILES, F.I.C.

(Concluded from p. 31).

THE solution of the cerium group of metals freed from thoria as described was then treated with an excess of sulphuretted hydrogen, and allowed to stand for twenty-four hours. The sulphide of lead was filtered off, washed, and the filtrate boiled till every trace of the hydric sulphide was expelled; the solution when cold was then made up to a volume of exactly 2 litres in a standard flask; 100.0 c.c. of the resulting solution thus equalled 2.0 grms. of the original nitrates, less the thoria which was removed. The following trials were made with this material:—(1st). In order to see whether a further treatment with a fresh supply of lead carbonate would yield any more precipitate, 100.0 c.c. were measured out, and treated with about 2 grms. more of the moist reagent with constant stirring for several hours. The precipitate was then collected on a filter, very thoroughly washed, dissolved in a little nitric acid, diluted considerably, and the lead precipitated by hydric sulphide. The sulphide of lead was filtered off, and the filtrate was evaporated to complete dryness, when only an unweighable stain was left in the basin. It was therefore seen that lead carbonate had now no action on the standard solution. (2nd). The amount of the total cerium group of oxides was determined by precipitation with only a *slight excess* of pure ammonium oxalate as follows:—Two portions of 100.0 c.c. were measured out into beakers, and each diluted with 100 c.c. of distilled water, raised to a boil, and then precipitated with a solution of 1.10 grms. of pure ammonium oxalate; after this the solutions were made *faintly* alkaline with ammonia,

and then allowed to stand for sixteen hours.* The highly crystalline precipitates were collected on ashless filters, washed, dried, and ignited over a powerful Bunsen flame till the weight remained constant.

	No. 1.	No. 2.
Cerium group oxides + crucible ..	27.6810	26.4660
Crucible	26.9065	25.6930

Grms. of ignited cerium groups oxides in 100.0 c.c. .. .	0.7745	0.7730
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Or a mean percentage of 0.7737 of cerium-yttrium oxides in 100 c.c. of the solution.

Measured portions of this were then taken and mixed with the same solution of "Thorium Nitrate Absol. Chem. Pur." already mentioned (p. 2). This solution contained per 100.0 c.c., 0.4765 gm. of ignited thoria and 0.0015 gm. of other oxides not precipitable by lead carbonate, but capable of being thrown down by ammonium oxalate.

100 c.c. of the cerium oxides solution and 100 c.c. of the thorium nitrate solution were mixed, and the whole treated with lead carbonate exactly as described in the preceding pages. The thoria was after the separation of the lead thrown down by ammonia and ignited, finally over the blast-lamp. The cerium oxide group was precipitated with a solution of 1.10 gm. of pure ammonium oxalate and the oxides ignited to a constant weight over a powerful Bunsen burner.

Then 100 c.c. of thorium nitrate solution and 50 c.c. of cerium oxides solution were treated precisely in the same manner, except that only half the amount of ammonium oxalate was employed. The volume of the solutions and the amount of wash-water used was kept as uniform as was possible. The following results were obtained:—

100.0 c.c. of thoria solution—	
Thoria	Found 0.476
	Theory 0.4765
100.0 c.c. of cerium solution—	
Ceric group oxides ..	Found 0.773
	Theory 0.7752
100.0 c.c. of thoria solution—	
Thoria	Found 0.4765
	Theory 0.4765
50.0 c.c. of cerium solution—	
Ceric group oxides ..	Found 0.3885
	Theory 0.3883

These results show that a very fair separation of the oxides can be obtained by only one treatment with lead carbonate, but it is obvious that it is easy after once precipitating the thoria to re-precipitate it after removing the lead with hydric sulphide with a fresh amount of the reagent. After the thoria has been ignited it is not an easy matter to re-convert it into the nitrate. The colour of some of the ignited thoria precipitates was noted:—

	Colour.
Thorium nitrate precipitated with ammonia .. .	Nearly white, but with a faint grey hue.
Thorium nitrate precipitated with lead carbonate ..	Almost pure white.
Thorium nitrate with 100.0 c.c. cerium solution ..	Faint brownish white.
Thorium nitrate with 50.0 c.c. cerium solution ..	Faint brownish white.

* Solubility of the Oxalates Precipitated as described.—In view of some other experiments on these separations, it was not without interest to ascertain what was the solubility of these oxalates precipitated as described; consequently the two filtrates and washings, amounting to 550 c.c., were mixed and evaporated in a platinum dish to complete dryness. When the volume of the hot solution was reduced to about 100.0 c.c. a film of oxalates began to separate out on the surface of the liquid, and on further evaporation a decided amount separated out. The whole was evaporated to complete dryness, and then ignited till all ammonium salts were expelled and the oxalates decomposed. The small amount of brownish oxides weighed 0.008 gm., from 4 grms. of nitrates, or 100 c.c. of the solution contain about 0.008 gm. of air-dried oxalates.

It has been noted that when the same solutions are precipitated respectively with ammonia and oxalic acid, that the ignited thoria from the oxalate is always of a much lighter colour than that which is obtained from the precipitation with ammonia. All the above four precipitates had a glassy crystalline appearance. As regards the colour of the precipitate it is stated (Truchot, "Les Terres Rares," p. 196) that "Thoria obtained by the calcination of the oxalate or the sulphate gives an absolutely white powder, while that obtained by the calcination of the hydrate gives hard and transparent fragments of a greyish brown colour," and Drs. Herzfeld and Korn (in their "Chemie der Seltenen Erden," p. 131) say of ignited thoria, "Dasselbe ist weiss bis grauget." It has been noticed that the manner in which the precipitate is ignited has a considerable influence on the final colour of the thoria. If the precipitate obtained with ammonia and dried in the air-bath at 120° C. is wrapped up in the filter-paper, and at first gently heated to char the paper and avoid projections, the resulting oxide always has a dark colour which even a long exposure to a powerful blast-lamp fails to remove entirely, while if the bulk of the dried precipitate is removed and ignited separately from the filter-paper the colour is always much lighter, and at times is almost snow-white. To clear up this doubt about the colour of ignited thoria precipitated by ammonia, fresh experiments are now being conducted on specially purified thorium nitrate.

In this connection it is well to remember that extremely small amounts of praseodymia, terbia, and possibly other members of the yttrium family, have the property of strongly colouring other oxides of the same group which, in a pure state, would give colourless oxides on ignition (Marc, CHEMICAL NEWS, vol. lxxxvi., p. 74).

Analyses of several minerals containing thoria have been made by this method. A compact mass of monazite of chocolate colour and apparently crystallised, which had a specific gravity of 5.129 and came from Arendal, yielded 8.20 per cent of thoria and a very distinct amount of uranic oxide.

Thorianite.—The writer is indebted to Prof. Wyndham R. Dunstan for a small specimen of this new and very interesting mineral, which has been examined for thoria by the lead carbonate process. The mineral was opened up by fusion with three times its own weight of sodium pyro-sulphate, as the fact that it was soluble in strong nitric acid or diluted sulphuric acid was at that time unknown to him.

The following results were obtained:

Analysis of Thorianite.	
Loss on ignition .. .	1.92
Silica	0.70
Lead oxide	3.21
Thoria	73.94
Zirconia	0.06
Cerium group oxides ..	2.74
Ferric oxide	3.22
Titanic acid	traces
Uranium oxide (U ₂ O ₃) ..	14.18
	99.97

These notes upon thoria will be supplemented by some remarks upon the separation of zirconia and ferric oxide by lead carbonate, and also by some notes upon the separation of cerium from lanthanum and didymium oxides.

Some New Dinaphthopyranic Nitrated Substances.

—A. Robyn.—When pyryl bromide reacts on aniline, ortho-, meta- and para-toluidine, and a naphthylamine, the author obtains a number of new mono- or dipyryl-nitrated substances which are derived by elimination of the hydracid either from equal molecules of the reacting substances, or from 1 molecule of the base and 2 molecules of pyryl bromide.—*Comptes Rendus*, cxli., No. 25.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JUNE 30TH, 1905.

By SIR WILLIAM CROOKES, F.R.S.,
and
SIR JAMES DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, July 10th, 1905.

SIR,—We submit herewith, at the request of the Metropolitan Water Board, the results of our analyses of the 227 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the Metropolitan Water Board taking their supplies from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 227 samples examined by us during the month, all were clear, bright, and well filtered.

The rainfall at Oxford during the month of June is the heaviest recorded since October, 1903; the amount actually measured was 4.15 inches. The average rainfall for the month is 2.10 inches; thus we have an excess of 2.05 inches, which cancels the previous deficit of 1.85 inches, and leaves an excess for the first six months of this year of 0.20 inch, or 1.8 per cent, on the thirty-five years' average.

Our bacteriological examinations of 395 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 787 others from special wells, standpipes, &c., making a total of 1182 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	206
New River, filtered (mean of 72 samples) ..	16
Thames, unfiltered (mean of 25 samples) ..	4493
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 198 samples) ..	38
Ditto ditto highest	242
Ditto ditto lowest	0
River Lea, unfiltered (mean of 25 samples) ..	264
River Lea, from the East London District clear- water wells (mean of 25 samples) ..	41
Kent District, from the wells at Deptford (mean of 25 samples) ..	1

Of the 320 daily samples taken from the general wells of the Metropolitan Water Board, fourteen samples, or 4.3 per cent, were sterile. Twenty-six samples, or 8.1 per cent, contained more than 100 microbes per c.c., and of these twelve samples contained more than 150 microbes per c.c. The twenty-six excess samples contained an average of 160 microbes per c.c. In May sixteen excess samples contained an average of 1.48 microbes per c.c.

It will be observed that, owing to the excess of rainfall, the microbic impurity of the raw Thames water in June has increased about four and a-half times what it was during the month of May, while the water of the Lea has been but little affected. The average of the filtered supply has also shown an increase of microbic impurity over that of the past month. This deterioration is shown by the fact that the percentage of samples containing more

than 100 microbes is nearly doubled as compared with the last month, and that twelve samples this month contain more than 150 microbes as compared with only five in the same condition in May.

The amount of organic matter in solution in the Thames-derived waters, has increased by about one-half, and their colour and the amount of oxygen absorbed is correspondingly greater. These variations we should expect from the fact that in the Thames valley during the month of June, the heaviest rainfall has been recorded since October, 1903.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

PROCEEDINGS OF SOCIETIES

THE FARADAY SOCIETY.

Ordinary Meeting, July 3rd, 1905.

Mr. W. R. COOPER in the Chair.

MR. SHERARD COWPER-COLES read a Paper entitled "*Some Notes on the Rapid Electro-deposition of Copper.*"

The reading of the paper was illustrated by lantern-slides, and the author exhibited specimens of copper sheets, tubes, and wire made by the "centrifugal" process.

The various processes for increasing the current densities in copper deposition by using mechanical means for keeping the copper smooth, are classified as follows:—

1. *Revolving or moving the cathode*, as in the processes of Wilde, Cotsworth, Wylie, and Grant. The current density employed is comparatively low.

2. *Burnishing the Copper during Electro-deposition (the Elmore Process)*.—The usual current density is under 20 ampères per square foot.

3. *Insulating the Growths on the Copper so as to Prevent further Increase*.—For example, the Dumoulin process in which sheepskin and other impregnators are employed. The current density is 35 to 40 ampères per square foot.

4. *Rapid Circulation of the Electrolyte*.—Examples: Thofehn's process, in which impinging jets are caused to play on the surface of a rotating cylinder (C.D. 50 to 100); Graham's process, in which the electrolyte is discharged on to a flat cathode surface (C.D. 300, just under the influence of the jets); Poore's process, in which the solution is sprayed on to the cathode, the stream forming the only electrolytic connection; Dessolle's process, used in Paris for coppering ornamental iron work; and finally, Harrison's, likewise an impingement process. The author considers that impingement processes are not likely to be applied commercially until the amount of solution circulated can be greatly reduced.

5. *Revolving Mandrel at a Critical Speed (Centrifugal Process)*.—This process has been developed by the author, and the latest methods of working are here described. The mandrels are suspended vertically, and are provided with Pelton wheels, which are driven by the electrolyte impinging against them. In the most recent form, however, a tubular vat is used, and hollow mandrels suspended on ball bearings, through the middle of which run the spindles. These are driven by a worm gearing from below. An 8-foot mandrel has only to be driven at about fifty revolutions per minute.

The author claims the following advantages: The copper is refined and manufactured into sheets or tubes in one operation, and is of a hard nature, similar to that which is cold-rolled; the process is at least ten times faster than any existing electrolytic process; a high current can be employed without deteriorating the quality of the copper; there is no risk of lamination; the plant is simple and

free from mechanical complications; the amount of copper locked up for a given output is small compared to other processes; finally, anodes of very impure copper can be used as compared to the anode copper used in other systems.

By using a mandrel in which a V groove has been indented, the spiral deposit that results can easily be pulled away, and then drawn down at once into wire, which can thus be made from crude copper in what is practically one operation.

The estimated capital expenditure and cost of working the "centrifugal" process are given in the paper.

Mr. A. STANLEY ELMORE (communicated) said the author had not mentioned heating the electrolyte as a method of accelerating the rate of deposition. He knew of one plant working the Wilde process in which the cathode was rotated rapidly, and the current density was by no means "comparatively low." He gave some further details regarding the Elmore process. The C.D. was occasionally pushed up to 30 amperes per square foot and has been carried up to over 200 amperes. A tensile strength as high as 42 tons per square inch had been attained. By the use of a burnisher the same high C.D. could be used with a less expenditure of power than in other processes, and he claimed that by a combination of burnishing and moderate circulation of electrolyte, better and more certain results could be obtained than by the author's "centrifugal" method. He asked how the author proposed to make tubes of less than 2½ inches diameter.

Mr. MILBOURNE said that all that was claimed for the "centrifugal" process had been borne out by the results of the trials he had made with a practical plant on the Continent.

Mr. W. C. PREBBLE pointed out that in the author's process the circulation of electrolyte took place just at the place where it was most needed, namely, the surface of the cathode.

Mr. J. V. MACKENZIE described an arrangement by which he had used current densities up to 45 on electrotyping work.

Dr. C. J. STEINHART said that capital expenditure was an all-important item; whether that required in the "centrifugal" process remained within the permissible limits remained to be seen. The author had successfully surmounted the "early stage" difficulties of his process.

Mr. T. C. CLOUD criticised the author's theory regarding the growth of nodules. He thought that the toughness of the metal was the result of the particles being drawn out into long fibres as they were being deposited.

Mr. COWPER-COLES replied to the various points raised. Tubes as small as 2½ inches could not be deposited, but could easily be drawn down.

A paper on "*The Use of Balanced Electrodes*," by Prof. W. W. HALDANE GEE, was read in abstract by Mr. R. S. HUTTON.

The method of ascertaining the weight of metal electrolytically deposited by directly weighing the cathode in the electrolyte instead of removing the cathode and weighing it—after washing and drying—is considered. The real weight (M) is obtained from the apparent weight (m)

by the formula $M = \frac{m \Delta}{\Delta - \delta}$; where Δ is the density

of the deposited metal, and δ that of the electrolyte. It is shown that since Δ occurs both in the numerator and denominator of the expression, that for most purposes it is not necessary to know the value of Δ with great accuracy. In the case of copper the value of Δ that may be used is 8.9. An ordinary physical balance is used, and a cylindrical cathode suspended by a thin wire passing through a hole in the bottom of the balance case is counterpoised in the electrolyte. The anode also is circular, and surrounds the cathode. Electrical connection is made to the cathode by a side wire whilst receiving a deposit, but is removed when the apparent increase of weight has to be ascertained. The method has been found very con-

venient in testing commercial types of ammeters. An accuracy of about 1 per cent can be generally obtained, and with a little care and by increasing the amount of deposit the accuracy can be brought under 0.5 per cent. In some experiments both sides of the balance may be used simultaneously when the electrochemical equivalents of metals in different combinations may be compared and current efficiencies ascertained. A number of experiments have been made with a mercury cathode and anode, the electrolyte being solutions of mercurous nitrate, or mercuric chloride mixed with potassium cyanide. The mercury cathode is enclosed within a shallow dish suspended in the electrolyte by a platinum wire. The anode is a layer of mercury at the bottom of the containing vessel. In the case of mercurous nitrate it is shown that the current efficiency as a monad is affected by the presence of mercuric and basic compounds. For good results the mercurous nitrate solution must be carefully prepared and a strong solution used.

Modifications of the method are described that may be used for the purpose of finding the density of electro-deposited metals, and for studying the relative loss and gain at anode and cathode.

Instead of an ordinary balance a spring balance may be substituted. The author also shows how a Nicholson's hydrometer may be used both as a cathode and as a means of finding the amount of deposit.

It is concluded that the method will be useful in the laboratory and test room as a means of rapidly arriving at results with sufficient accuracy for many commercial purposes.

Dr. F. M. PERKIN said that the drawback to the use of mercury was that only small currents could be measured therewith. What was particularly wanted was an instrument that would indicate continuously; for example, the cathode might be suspended in a helix, to which a pointer was attached, as in the Ayerton-Perry meters.

Mr. H. D. LAW and Dr. F. MOLLWO PERKIN contributed a paper on "*The Electrolytic Oxidation of Hydrocarbons of the Benzene Series*. Part II. *Ethyl Benzene, Cumene, and Cymene*." (Will be inserted in full).

Mr. H. D. LAW and Dr. F. MOLLWO PERKIN also presented a note on "*The Electrolytic Analysis of Antimony*."

Some little time ago, requiring to carry out a number of antimony determinations, we thought the simplest and most easy way would be to employ electrolytic methods. At first we used the method of Classen, in which the antimony salt is dissolved in sodium sulphide. This process works extremely well, and the appearance of the deposited metal leaves very little to be desired. We found afterwards, however, that the method suggested by Fischer (*Ber.*, xxxv., 2348), in which small quantities of potassium cyanide are added to the sodium sulphide solution, yields even better results. From the point of view of accuracy of working there is no exception to be taken to the method. But the preparation of the sodium sulphide, which has to be practically saturated at the ordinary temperatures and preserved in well-stoppered bottles in a cool place, is very troublesome. We therefore endeavoured to find a method which would give accurate results, and which could be carried out at once without the trouble of preparing any special reagents.

Good results had already been obtained in this laboratory with tartrate solutions in the case of nickel, cobalt, and iron, and remembering how readily antimony salts dissolve in tartaric acid we naturally turned to it. This solution has already been tried, but apparently the results have not been found satisfactory, owing to the length of time which is supposed to be required.

In "*Electrolytic Methods of Analysis*," by B. Neumann, p. 145, the following remarks are made with reference to solutions in tartaric acid:—

"The electrolysis of a solution of antimonyl potassium tartrate, or of an antimony solution containing tartaric acid, yields a deposit which is entirely satisfactory; the

electrical resistances of these solutions are, however, so great (as with all other solutions containing chiefly tartrates) that the separation takes place too slowly for practical use."

We have not found solutions of tartrates to have a high electrical resistance, as will be seen from the table below. The resistance of a solution of tartaric acid is indeed rather high, owing to its slight ionisation, but that is not the case with ammonium or other alkali tartrates.

The following table shows that with hot solutions very good results can be obtained by using a solution of an antimony salt containing from 6—8 grms. of ammonium tartrate to each 120 c.c. of solution, and further, that the whole of the antimony can be deposited out in from three to five hours.

Sub- stance.	Tem- perature.	Time in hrs.	C.D. in sq. decm.	E.M.F. Volts	Deposit.	Per- centage Sb.	Theo- retical per- centage.
Grms.			Ampères.				
1'07624	70-80	6	0'2-1'0	3'0-3'5	0'3882	36'08	36'16
1'07624	Cold	*	0'2-0'5	2'6-3'2	0'3902	36'26	36'16
1'07624	Cold	*	0'2-0'4	2'7-3'1	0'3890	36'16	36'16
1'07624	60-70	4	0'2-0'6	3'0	0'3900	36'24	36'16
1'0350	65-75	5	0'2-0'5	3'1	0'3736	36'10	36'16
1'0350	70-80	4'5	0'3-0'8	3'0-3'4	0'3762	36'34	36'16

* Over night.

The deposits from hot solutions adhere to the cathode with great firmness. But from cold solutions, unless low-current densities are employed, the deposited metal is apt to be crystalline, or to be of a brittle nature and to exfoliate. Cold solutions, in fact, cannot be depended upon, although the appearance of the deposited metal is superior to that which is obtained from hot solutions. From hot solutions there is a tendency for the metal to have a slightly brown shade, although at times it is quite white. The addition of 1 gm. of tartaric acid to the electrolyte tends to improve the appearance of the deposit, and also prevents the tartrate solution from darkening.

In view of the trouble of preparing the sodium sulphide solutions we certainly think that this method is to be recommended, more especially as the results which we have obtained are very satisfactory from an analytical point of view.

Mr. J. H. BELCHER said that he had used the ammonium tartrate solution with success.

Mr. R. S. HUTTON and Mr. J. R. BEARD communicated some "Notes on Heat Insulation, particularly with regard to Materials used in Furnace Construction." (Will be inserted in full).

Mr. R. W. VICAREY presented a paper entitled "Storage Batteries and their Electrolytes," which was taken as read.

This is a paper intended by the author to be a *résumé* of observations and experiments referring to the deleterious effect of nitrogen compounds (especially ammonia) upon the durability, efficiency, and behaviour of storage batteries.

The paper deals with the action of ammonia and other nitrogen salts, and the salts of potassium, sodium, aluminium, magnesium, and calcium, and it discusses their uses in the various manufacturing processes. It also deals with the waters and acids used for the electrolytes of batteries.

It would appear that ammonia must be considered as a dangerous impurity, the total absence of which, however, cannot be absolutely insisted upon. The presence of ammonia in the surroundings or neighbourhood of the cell must be carefully guarded against, and the percentage actually present in the cell must be kept as low as possible by the use of waters and acids of the purest quality.

The author points out that above certain limits of ammonia little difference is observed in the behaviour of cells, but below that limit much difference occurs. Thus experiments upon cells containing proportions of ammonia varying from 10 per cent to 0.1 per cent (70.40 to 70.4 grains per gallon), the loss in capacity was 22 to 31 per cent immediately after the addition of the ammonia, whilst cells containing less than 0.1 per cent did not drop in

capacity immediately, but varied intermittently from 10 to 15 per cent, finally settling at the end of eight months to a permanent loss of 15 to 22 per cent.

From the data given it appears that ammonia is very slow in its action before it makes any appreciable or apparent loss in the capacity of the cells, the average time being about twelve months, dating from the initial charge.

The effects of ammonia in its various combinations appear principally in two distinct forms: (1) it causes an excessive disintegration or shedding of active material at the positive (PbO_2) plate; (2) it becomes deposited upon the negative (spongy) plate, and finally closes up the pores of the active material, thereby causing a decrease in the ampère-hour capacity or efficiency varying from 10 to 60 per cent in about twelve months.

The use of water taken from the steam boiler and termed "distilled" is mentioned as a dangerous practice that is common in central stations, &c.

The position of the battery and its surroundings are also touched upon.

Finally, it is proposed that a series of experiments be carried out upon some cells in an attenuated atmosphere, away from all manufacturing districts.

Prof. E. WILSON presented a paper on "Alternate Current Electrolysis." This was taken as read, and the discussion postponed until the autumn.

NOTICES OF BOOKS

Précis d'Analyse Chimique Quantitative. ("Compendium of Quantitative Chemical Analysis"). By E. BARRAL. Paris: J. B. Baillière et Fils. 1905.

THIS book gives a very systematic course of analytical chemistry, and is so complete that a student who works through it, aided by a little personal direction by a teacher, should become thoroughly well grounded in the essentials of quantitative analysis. The discussion of general methods is a particularly satisfactory feature of a book which leaves little to be desired in any respect. Some organic analysis is included, methods of estimating the most important substances used in pharmacy, medicine, &c., being shortly described, though no technical analyses are contained in the book. The short account of electrolytic methods might with advantage have been somewhat enlarged, more especially as regards the manipulation and chemical details of the processes, which are not described nearly so fully as the apparatus employed, but on the whole the careful choice of the methods advocated and the succinctness and clearness of the author's language are points which win for the book a confident recommendation as an unpretentious and yet eminently useful text-book of chemical analysis.

Leçons sur la Théorie des Gaz. ("Lessons on the Theory of Gases"). By L. BOLTZMANN. Translated by A. GALLOTTI and H. BÉNARD. Part II. Paris: Gauthier-Villars. 1905.

ALTHOUGH it is now nearly ten years since the first part of Boltzmann's "Vorlesungen Über Gastheorie" appeared, it still maintains its position as one of the most valuable among similar text-books, and a translation of it will no doubt be acceptable to French readers. This second part treats of the theory of Van der Waals, gases with polyatomic molecules, and the theory of dissociation, and contains a bibliography of the principal books and articles on the theory of gases which have appeared since the publication of Boltzmann's book. As in the first part valuable expository notes have been added by Professor Brillouin, of the Collège de France, and the original has lost none of its characteristic clearness and lucidity in the translation.

Transactions of the American Electrochemical Society.
Volume VI. Philadelphia: The American Electrochemical Society. 1904.

THIS volume contains the papers which were read before the Sixth General Meeting of the American Electrochemical Society, held at St. Louis in September, 1904, and also those which were read and discussed in joint sessions of Section C. of the Fifth International Electrochemical Congress and the American Electrochemical Society. Amongst the great variety of subjects treated in the book it is difficult to single out any paper as more particularly worthy of notice, especially when the general level of interest is so high, but the following must be mentioned as deserving the careful attention of all who are interested in electrochemistry, viz.:—The paper by Professor Richards, of Harvard, on "The Relation of the Hypothesis of Compressible Atoms to Electrochemistry," that by Dr. Hans Goldschmidt on "Aluminothermics," which gives an interesting account of the properties and use of "thermit," and J. Sigfrid Edström's paper on the "Electrical Extraction of Nitrogen from the Air."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxi., No. 25. June 19, 1905.

Preparation and Properties of Azotyl Fluoride.—Henri Moissan and Paul Lebeau.—The authors show that fluorine does not act on nitrous oxide and nitrogen peroxide at ordinary temperatures, and that a new gaseous compound, azotyl fluoride NO_2F , is produced with nitric oxide. This gas has density 2.24. Its fusion-point is -139° and its boiling-point -63.5° . It possesses great chemical activity. It does not, however, combine at ordinary temperatures with hydrogen, sulphur, and carbon, but unites with boron, silicon, phosphorus, arsenic, antimony, and iodine. It decomposes cold water with production of hydrofluoric and nitric acids, and it reacts on a large number of organic compounds, and in all these reactions it acts by its own fluorine and the group NO_2 .

Alcyl Thuyones and Compounds of Thuyone with Aromatic Aldehydes.—A. Haller.—Thuyone contains a

complex $\begin{array}{c} \text{CO} \\ \diagup \\ \text{CH}_2 \end{array}$, in which the group CH_2 lends itself to

substitutions analogous to those which the author obtained with menthone and methylhexanone, and also to condensations with the aromatic aldehydes. The thuyone used for the preparation of the various derivatives distilled at 84° under 13 m.m. pressure, was of density 0.9206, and had rotatory power $[\alpha]_D = +74.30^\circ$.

A Basic Ferric Sulphate.—A. Recoura.—During his researches on ferric sulphate the author isolated a basic sulphate whose composition is interesting because it throws light on the constitution of the hydrated ferric salts. This basic salt plays an important part in the phenomena which take place in solutions of ferric sulphate during their evaporation for the isolation of this hydrated sulphate. When obtained pure it is in the form of a yellowish white powder very soluble in water, and having the composition $6[\text{Fe}_2\text{O}_3, 3\text{SO}_3], \text{Fe}_2\text{O}_3$.

Chemical Properties of the Anhydrous Chloride of Neodymium.—Camille Matignon.—A systematic investigation of the chemical properties of neodymium chloride leads to the preparation of a crystalline oxychloride by two distinct methods in the same manner as in the preparation of the bromide and iodide of anhydrous neodymia. The action of hydrogen on this compound

shows an important difference between neodymium and the neighbouring element samarium.

A Method of Determining the Specific Heats of Solutions. Molecular Heat of Good and Bad Electrolytes.—P. Th. Muller and C. Fuchs.—Good electrolytes are distinguished from other substances in aqueous solution by a number of properties. The authors determine their specific heats by the method of electrical heating rather than by the ordinary method to avoid the considerable variation of temperature.

Researches on Mercury Formates.—Raoul Varet.—The author's experiments on mercury formates explain the rapid transformation of mercuric formate into mercurous formate, formic acid, and carbon dioxide, a reaction which evolves $+53.2$ cal. In the same way the decomposition of mercurous formate into liquid mercury, liquid formic acid, and gaseous carbon dioxide liberates $+20.7$ cal. Of the various methods of decomposition of this salt that can be imagined, this is the one corresponding to the thermic maximum.

MISCELLANEOUS.

Sir William and Lady Crookes propose leaving London at the end of July, to attend the meeting of the British Association in South Africa. They expect to return home about the middle of October, and hope correspondents and friends will consider their absence a sufficient excuse for any delay which may arise in replying to letters.

Society of Chemical Industry.—The President (Dr. W. H. Nichols) and the members of the Society of Chemical Industry of the British Empire and America, as part of the programme of their convention in London, paid a visit of inspection on Saturday to the works of Burroughs Wellcome and Co. After inspecting the "Kepler" and "Tabloid" buildings, the party was joined by a number of distinguished medical and other guests, amongst whom were Sir Patrick Manson, Lady Manson, Sir James Dick, Professor H. E. Armstrong, and Mr. R. A. Robinson, L.C.C. (President of the Pharmaceutical Society of Great Britain), and adjourned to the Wellcome Club and Institute, founded for the benefit of the firm's employees. Here luncheon was served to two thousand guests in a special marquee, after which a *fête* was held in commemoration of the completion of the firm's quarter century of work. Cablegrams of good wishes to the Society of Chemical Industry and congratulation to the firm were received from its branches and agents in Sydney, Cape Town, Milan, Constantinople, Mannheim-Waldhof, West Indies, Vienna, Berlin, Charlottenburg, Switzerland, Montreal, Calcutta, Shanghai, Persia, Amsterdam, New York, Brussels, Liège.

ST. PAUL'S SCHOOL, West Kensington.—

An EXAMINATION will be held at the above School on Tuesday, September 5th, 1904, and on the following days, for filling up about Twenty Vacancies on the Foundation.—Full particulars of the Examination can be obtained on application to the Bursar.

TO BE SOLD, the English Patent referring to Apparatuses for Wound Impregnation (mining) applicable to Tar Distillation and Founding, &c. Thirty-six installations have been started in Germany, with large profits.—For particulars address, in German, "K.D. 3573," Rudolf Mosse, Cologne.

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TABLE OF RARE ELEMENTS.

By E. L. N. ARMBRECHT.

Symbols, Atomic Weight, Discoverer, Isolater, Specific Gravity, Principal Source, Melting-point, Properties, Salts of, Price, &c.,

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Mme. CURIE'S Thesis

ON

RADIO-ACTIVE SUBSTANCES.

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THE CHEMICAL NEWS.

VOL. XCII., No. 2383.

COLOURS IN METAL GLASSES, IN METALLIC FILMS, AND IN METALLIC SOLUTIONS.*

By J. C. MAXWELL GARNETT.

IN the first section of this paper it is pointed out that one and the same metal may cause a great variety of different colours, just as the colour of gold vapour differs from the colour of the light reflected from gold as well as from the colour of the light transmitted by gold leaf. While the ultimate cause of the colour of a metalliferous medium is to be found in the structure of the metal molecule itself, the arrangement of these molecules, according to any fixed law, causes them to affect one another's free periods in a definite manner, and thus gives rise to corresponding optical properties. The object of this paper is to discover, by means of these optical properties, the molecular arrangement (microstructure) of various metal glasses, of colloidal solutions of metal, and of metallic films.

Expressions giving the refractive index and the absorption coefficient (the optical constants) of a compound medium consisting of metal (ϵ) in small spheres (granular), and (ϵ in discrete molecules (amorphous), diffused through an isotropic non-dispersive transparent medium (the solvent), are next investigated in terms of the corresponding optical constants of the normal metal.

The particular formulæ which apply when the volume proportion of metal in the compound medium is small, as in the case of metal glasses and of "colloidal solutions" of metal in water, are also obtained, and it is found that while spheres of any metal, so diffused that there are many to a wave-length of light, will produce colours which vary with the refractive index of the solvent, diffused molecules of any metal produce, by transmitted light, a colour (the vapour colour) which is independent of that refractive index.

By means of these formulæ and of the optical constants of gold, silver, and copper, experimentally determined for monochromatic light of several different wave-lengths, the numerical values of the corresponding optical constant which would be possessed by diffusions of spheres and of molecules in glass, water, or vacuum, are calculated and tabulated. Defining the absorption of light of wave-length λ by any absorbing medium as being the logarithm of the ratio of the intensities of that light before and after traversing a unit-length of the medium, graphs are given of the calculated absorptions of these diffusions. Curves are also shown representing the absorptions of specimens of gold ruby glass, of silver stained glass, and of copper ruby glass, as measured at the National Physical Laboratory.

A comparison of these curves with the graphs for gold spheres and for gold molecules in glass, and a collation of the results with others already obtained in a previous communication (*Phil. Trans.*, A, 1904, pp. 385 to 420), leads to the conclusion that the colour of gold ruby glass is due primarily to the presence of small spheres of gold. The irregular blue and purple colours sometimes exhibited by gold glass are then explained by the presence of crystallites caused by the coagulation of the gold spheres. Again, when the corresponding graphs with water as solvent are compared with the absorptions of colloidal gold as measured by Felix Ehrenhaft (*Ann. der Phys.*, 1903, vol. xi., p. 489), little doubt remains but that colloidal gold consists of small spheres in suspension; the blue colour produced by particles coarser than the small spheres is, as

in the case of glass, due to the red light being reflected by the crystallites and so not transmitted.

The close similarity between the observed absorptions of yellow glass stained with silver, and the calculated absorptions of a diffusion of silver spheres in glass—the calculated absorptions of a diffusion of silver molecules in glass are quite different—indicates that the stained region must contain small spheres of silver. Ehrenhaft's description (*loc. cit.*, p. 507) of the nature and position of the absorption band observed in the spectrum of colloidal solutions of silver, describes so well the position of the absorption band determined by calculation for a diffusion of silver spheres (but not of silver molecules) in water, as to justify the conclusion that the bulk of the silver present in colloidal solution is in the form of small spheres: little if any being in true solution (*i.e.*, molecularly subdivided); and this conclusion is confirmed by the fact that the refractive index of a colloidal solution of silver, which was measured by Barus and Schneider (*Zeit. f. Phys. Chem.*, vol. viii., p. 278), is precisely that which calculation shows to be possessed by a diffusion of silver spheres (but not of molecules) in water.

Measurements, made by Sir William Abney, of the intensities with which light of various wave-lengths is reflected from the interface between the stained and unstained regions of one of the specimens of silver glass which had belonged to Stokes, when held with the stain turned away from the source of light, are in general accordance with the reflective powers calculated on the hypothesis that small spheres of silver are distributed throughout the stained regions, the maxima corresponding to light of wave-length about $\lambda = 0.436$ in both cases. If the silver in the glass had been molecularly subdivided the maximum would have been at about $\lambda = 0.360$. The presence of silver spheres (but not of discrete molecules of silver) throughout the stained region thus accounts for the blue reflection, in accordance with Stokes ("On the Change of Refrangibility of Light," *Phil. Trans.*, 1852; "Collected Papers," vol. iii., p. 316), as well as for the amber colour of silver glass viewed by transmitted light, proving that both colours were due to suspended particles of silver.

A comparison of the observed absorptions of copper ruby glass with the calculated absorptions of copper spheres and of copper molecules diffused in glass, shows that copper ruby glass owes its colour to the presence in the glass of small spheres of metallic copper,* while some copper molecules are probably also present. Although it has thus been proved that gold and copper ruby glasses and silver glass owe their colours to diffused spheres of the metal, the metals which colour some other glasses cannot be present in the metallic form; for example, the deep blue colour of cobalt glass cannot be due to diffused metallic cobalt, which, according to calculation, would give a reddish colour by transmitted light akin to that observed by Ehrenhaft (*loc. cit.*, p. 506) in a "colloidal solution" of that metal.

The colours produced in gold, silver, and soda glasses by the radiation from the emanation from radium, give rise to the suggestion that all glasses contain free ions of metal, and it is by the discharge of these ions and the consequent reduction of the metal (so that the metal is diffused in the glass), that cathode and Becquerel rays are able to colour the glasses.

Expressions are obtained giving the absorptions and reflective powers of amorphous or granular forms of gold and silver, the specific gravity of which is any proper fraction, μ , of that of the metal in its normal state. Curves are constructed to show how the values of these expressions, and thus also the colours exhibited by transmitted and by reflected light, vary with μ .

A comparison of these calculated colour changes with those actually shown by gold and silver films, such as those deposited on glass by Faraday (Bakerian Lecture, *Phil.*

* Stokes (*loc. cit.*, vol. iv., p. 245) thought copper ruby glass was coloured by suboxide of copper, and attributed the change of colour in some specimens to suspended particles of the metal.

* Abstract of a Paper read before the Royal Society, June 8, 1905.

Trans., 1857), and by Beilby (Hurter Memorial Lecture, Glasgow, 1897), when subjected to heat and to pressure, indicates that (a) the films as first prepared are in the amorphous or granular phase, and (b) heating diminishes the density of the film, while pressure is able to increase that density again, and finally (c) this diminution of density is probably effected by the passage of metal from the amorphous to the granular phase, and by the growth of the larger granules at the expense of the smaller, while increase of density is accomplished by changing some of the metal from the granular to the amorphous phase.

The optical properties of Carey Lea's (*Amer. Journ. Science*, 1889, and *Phil. Mag.*, 1891) so-called solutions of allotropic silver show that they consist of small spheres of silver in suspension in water. From this and other evidence it is shown that the suggestions made in the former paper (*loc. cit.*, p. 419) that Carey Lea's silver was not allotropic, but consisted of normal silver in a finely divided (but not necessarily granular) state, was almost certainly correct.

The three forms of silver discovered so long ago as 1861 by Hermann Vogel (*Pogg. Ann.*, 1861, vol. cxvii., p. 316), were probably the amorphous, granular, and crystalline forms discussed in this paper.

The paper concludes with the suggestion that many forms of metals which have hitherto been considered to be allotropic, because possessing optical properties distinct from those belonging to the metal in its normal state, are merely cases of fine division. Thus the properties of Bolley's lead (*cf.* Roberts Austen, "Metallurgy," p. 90), of Schützenberger's (*Bull. Soc. Chim.*, 1878, vol. xxx., p. 3) silver and copper, and of other alleged cases of allotropy cited by Roberts Austen (*loc. cit.*), do not require the postulation of an allotropic molecule for their explanation.

ACTION OF AMMONIA AND OXIDISING AGENTS ON METALS.

By Dr. HODGKINSON and A. H. COOTE.

IN the *British Association Report*, Section B, Cambridge Meeting, 1904, we read a short note on the "Action of Ammonium Nitrate on some Metals."

As it appeared to be to some extent a case of oxidation of the metal at the expense of the nitric oxygen and the solution of the metallic oxide, or hydroxide, in ammonia, we have, since publishing that note, made a number of experiments with other oxidising substances than the oxygen of the NO_3 group in the presence of considerable amounts of ammonium hydroxide.

It occurred to us that the simplest oxidising substance we could employ would be hydrogen peroxide. Many metals are most vigorously attacked by hydrogen peroxide under ordinary conditions. The case of iron is well known.

In one set of experiments we have employed hydrogen peroxide (commercial 20 vols.) mixed with an equal volume of 0.8800 ammonia solution. In this we have immersed weighed amounts of metals for a definite time, and of approximately the same area. As in the case of the ammonium nitrate experiments, we commenced with cadmium. Our results at present are expressed in percentage loss in a definite time—five minutes in this case.

Cadmium, 32 sq. c.m., 1.795 grms. Lost 7 per cent.
Copper, 30 sq. c.m., 7.64 grms. Lost 1.4 per cent.
Copper (2), 32 sq. c.m., 1.37 grms. Lost 3.6 per cent.
Iron. Absolutely no action.
Zinc, 32 sq. c.m., 1.79 grms. Lost 3.9 per cent.
Copper-nickel alloy, 32 sq. c.m., 13.51 grms. Lost (about) 0.1 per cent.

We also give two results with cadmium and copper-nickel in a solution of ammonium nitrate to which ammonium hydroxide and hydrogen peroxide was added.

Cadmium, 32 sq. c.m., 1.672 grms. Lost 18 per cent.
Copper-nickel, 32 sq. c.m., 13.51 grms. Lost 1.0 per cent.

The much increased action of the ammonium nitrate solution, to which hydrogen peroxide had been added, on metals is perhaps explicable. When metals dissolve in ammonium nitrate solution alone we have shown that nitrites are formed (British Association, 1904). When hydrogen peroxide is present a nitrite does not appear to be formed. In fact a sodium nitrite solution, to which ammonia and hydrogen peroxide were added, did not give the α -naphthylamine sulphanilic acid test for nitrous acid.

THE RELATIVE PROPORTION OF RADIUM AND URANIUM IN RADIO-ACTIVE MINERALS.

By E. RUTHERFORD and B. B. BOLTWOOD.

THE experiments made by one of us (Boltwood, *Phil. Mag.*, 1905, [6], ix., 599), have shown that within the limit of experimental error the amount of radium present in radio-active minerals is proportional to the content of uranium. The amount of radium corresponding to each gm. of uranium in a mineral is thus a definite constant which is of considerable practical as well as theoretical importance.

The proportionality between the content of uranium and radium in radio-active minerals strongly supports the view that radium is a decomposition product of uranium. According to the disintegration theory, the amount of radium per gm. of uranium present in a mineral should be a constant whose value can be approximately deduced if the relative activity of pure radium and pure uranium is known.

In order to determine the amount of radium associated with one gm. of uranium it is only necessary to compare the activity of the emanation produced by a standard quantity of pure radium bromide with that produced by a quantity of mineral containing a known weight of uranium.

In the experiments which are to be described, a standard solution of radium bromide was prepared from a specimen of radium bromide, which had been found experimentally by Rutherford and Barnes to give out heat at a slightly greater rate than 100 gm.-calories per hour. The radium bromide was, therefore, probably pure. About 1 m.grm. of the salt was taken and weighed as accurately as possible on a balance. The weighing was confirmed by comparing the relative gamma-ray effect produced on an electroscope by the sample in question and the effect produced by a quantity of radium bromide weighing 23.7 m.grms. The determinates by the two methods were found in good agreement.

The known weight of radium bromide was dissolved in water and solutions were successively made up which contained 10^{-2} and 10^{-4} m.grm. of radium bromide per cubic centimetre. Of the more dilute solution a quantity equivalent to 1.584 c.c. was carefully weighed out, transferred to a glass bulb having a capacity of about 100 c.c., and diluted to a volume of about 50 c.c. with pure distilled water. The bulb was sealed and allowed to stand for about sixty days in order that the maximum quantity of emanation might accumulate. At the end of this period the emanation was completely removed by boiling the solution and was transferred to an air-tight electroscope, in which its activity was measured. The observed activity corresponded to the emanation from 1.584×10^{-4} m.grm. of radium bromide, which was assumed to be equivalent to 0.926×10^{-4} m.grm. of radium.

The activity of the maximum or equilibrium quantity of emanation produced by the radium associated with 1 gm. of uranium in a radio-active mineral was determined by the method which has already been described (Boltwood, *loc. cit.*). The mineral chosen was a very pure sample of uraninite from Spruce Pine, N.C., containing 74.65 per cent of uranium.

The activity of the emanation from the standard radium bromide solution was equal to 24.24 divisions per minute. The activity of the emanation from 0.1 gm. of the mineral was equal to 14.45 divisions per minute, corresponding to 193.6 divisions per minute for each gm. of uranium present. These values indicate that the quantity of radium associated with 1 gm. of uranium in a radio-active mineral is equal to approximately 7.4×10^{-1} gm. One part of radium is therefore in radio-active equilibrium with approximately 1,350,000 parts of uranium.

By the application of these numbers to the ordinary ores of uranium it is possible to determine their actual content of radium. Thus a high-grade pitchblende ore containing 60 per cent of uranium carries approximately 0.40 gm. of radium, equivalent to 0.69 gm. of radium bromide, per ton of 2000 pounds. A low-grade 10 per cent uranium ore will contain per ton approximately 0.067 gm. of radium, equivalent to 0.115 m.grms. of radium bromide.

The amount of radium occurring with uranium is about the amount to be expected if uranium is the parent of radium, but a satisfactory comparison of theory with experiment is not possible until the relative activity of pure radium and pure uranium is more accurately determined. Experiments in this direction are in progress and the results will be given in a later paper. A method has been devised for determining in a radio-active mineral the proportion of the total activity due to the presence of uranium, radium, and the other radio-active bodies. The results obtained lead to the conclusion that actinium is not a direct product of uranium in the same sense as is radium. An account of these experiments will be published later.—*American Journal of Science*, xx., No. 115.

PRELIMINARY OBSERVATIONS ON RADIO-ACTIVITY AND THE OCCURRENCE OF RADIUM IN AUSTRALIAN MINERALS.*

By D. MAWSON, B.E., Junior Demonstrator in Chemistry,
and
T. H. LABY, Acting-Demonstrator in Chemistry in the
University of Sydney.

Literature.

PROFESSOR H. BECQUEREL, as is well known, was the first to observe what is now called radio-activity in uranyl-potassium sulphate. Schmidt extended the observations to thorium minerals (*Wied. Annal.*, 1898, lxx., p. 141). Madame Curie (*Comptes Rendus*, 1898, cxxvi., p. 1601), who independently made the same discovery, has published values of the radio-activity of thirteen minerals (Thesis présentée à la Faculté des Sciences de l'Université de Paris) of high uranium and thorium content, as measured by the ionisation produced in an air gap. Sir W. Crookes (*Proc. Roy. Soc.*, 1900, lxxvi., p. 409) looked for radio-activity by a photographic method in his collection of minerals, especially among the barium ones; but found only euxenite, alvite, arrhenite, sipilite, and hiebnite to be active. These minerals contain either uranium or thorium. No instance of the comparatively intense activity of minerals containing these elements has been found in their absence. The Hon. R. J. Strutt (*Proc. Roy. Soc.*, 1904, lxxiii., p. 193) examined the activity of samarskite, fergusonite, pitchblende, malacone, monazites, and zircon by a different method, depending on the rate of decay of the activity of the gas given off when the minerals were heated.

American uranium bearing minerals were examined by B. B. Boltwood (*Am. Journ. Sci.*, 1904, xviii., p. 97) for radium, and it was found that in uraninite, gummite, uranophane, and samarskite, the radium present as indicated by the emanation method was proportional to the

uranium content. This does not appear to hold, for the uraninite and samarskite examined by Strutt for the former was only half as active as the latter, and this would scarcely be the ratio of the uranium in the two minerals. More recently (*loc. cit.*, p. 378) he has studied the radio-activity of natural waters. Radium has been found by Obalski (*Eng. and Min. Journ.*, March 17, 1904) to occur in a cleveite and in a bituminous substance from Quebec, containing uranium as an impurity. Elster and Geitel (*Phys. Zeit.*, 1903, v., p. 11) have detected radio-activity in fine mud from the Italian watering place Battaglia. Radio-activity was detected in natural gas by E. F. Burton (University of Toronto Studies—Physical Science Studies). An examination of the radio-activity of Russian muds was made by J. Borgmann (*Nature*, 1904, lxx., p. 80). A radio-active gas was found in the soil and water near New Haven, U.S.A., by H. A. Bumstead and L. P. Wheeler (*Am. Journ. Sci.*, 1903, xvi., p. 328, and 1904, xvii., p. 97). Later Mr. Bumstead published an account of atmospheric radio-activity (*loc. cit.*, xviii., p. 1).

M. F. Pisani (*Bull. Soc. Franc. de Minéralogie*, 1904, Part I., xxvii., p. 58) has recently examined by photographic methods a large number of diverse types of minerals, in all about 77, and found that in every case those containing uranium or thorium were active; exceptional cases were certain specimens of fluorspar, which from his results appear to act comparatively strongly on the photographic plate. Specimens of fluorspar from the same districts were tested in our apparatus, and gave negative results. M. G. Bardet (*Bull. Soc. Franc. de Minéralogie*, 1904, Part I., xxvii., p. 63) arranges a number of the more common uranium and thorium minerals in a comparative table, according to the activity exhibited photographically. R. W. Brocke (*Eng. and Mining Journ.*, June 2, 1904) has published a comparative table of activities measured by a simple type of electroscope.

Experimental Methods.

A preliminary examination of a number of the minerals was made photographically, and the active ones were readily detected. No disagreement was found between the photographic and the electrical methods. Since the β - and γ -rays are the photographically active ones, it is an unsafe method, as Rutherford has pointed out, to rely on alone. Our results, as stated in the table, were obtained by the use of a C. T. R. Wilson's electroscope (*Proc. Camb. Phil. Soc.*, 1903, Part II., xii.), consisting of a rectangular brass box, with a narrow gold leaf, insulated throughout with sulphur, and made by one of us in the Engineering Laboratory. The plate potential used was about 209 volts (as measured by a static voltmeter of the Physics Department), which gave the maximum sensitiveness. The case was preserved throughout at a constant sensitive angle of tilt. The movement of the gold-leaf was read by means of a microscope moved by a screw thread. The leaf was connected to the upper of two insulated brass plates 11 c.m. in diameter separated by a 5 c.m. air gap, and surrounded by a metal case which was earthed. The lower of the plates was kept at a positive potential of 300 volts, by means of a battery of test-tube accumulators, which was found sufficient to produce a saturation current. On this plate the mineral was placed in a circular lead dish of 5 c.m. diameter, 3 m.m. in depth—a fresh one being used for each mineral.

As Madame Curie found that the activity of uranium oxide U_2O_5 was constant for a period of five years, we compared the current passing when the mineral was tested with that from uranium oxide, the same standard specimen being used for each comparison. This was done by observing the time with a stop-clock, when the leaf took to fall through the same distance, first which the mineral then with the U_2O_5 . In all cases the minerals were finely ground, and the lead dish completely filled and levelled off.

In examining the emanation from several specially selected minerals, about 40 grms. of the finely powdered substance was heated in a porcelain tube in an organic

* Read before the Royal Society of N. S. Wales, October 5, 1904. From the *Journal and Proceedings of the Royal Society of N. S. Wales*, vol. xxxviii.

combustion furnace to the highest attainable temperature. The tube was pumped out whilst thus heated, allowed to fill, and air drawn over from the other end, and again pumped out. The gas from the Sprengel pump was collected over mercury, and transferred to a partially evacuated metal vessel, of about 800 c.c. capacity, with a central insulated wire. The gas in the vessel was brought to atmospheric pressure by the addition of air. The walls of the vessel were kept at a positive potential of 300 volts, and the current through the gas to the wire, attached to the gold leaf of the Wilson electroscope, charged it positively with resulting fall of the leaf.

Measurements were taken over a period of four days and the results plotted. Decay of the radio-activity of the emanation to half its initial value in four days indicates, as shown by Rutherford and Soddy, the presence of radium. Our instrument was not suited for measuring the decay of the thorium emanation. In this work Rutherford's "Radio-activity" was found most useful, especially the chapter on methods of measurement.

Results.

A large collection of minerals was examined, and as expected, only those containing uranium or thorium were found to have measurable activity. The apparatus readily detected an activity of $\frac{1}{250}$ that of U_2O_5 . Among the minerals tested and found to be inactive the following are worthy of mention:—

Columbite, Barrier Ranges, N.S.W.	} Various localities.
Stibiotantalite, Greenbushes Tin-field, W.A.	
Zircon	
Tellurides	
Bismuth ores	
Tin stones	
Barytes	

As will be noticed in referring to the following table, only two occurrences of uranium minerals have been recorded, so far as we are aware, in Australia. In both cases specimens at hand, up to the present time, are too small to admit of complete investigation. The first is a *euxenite* occurring with stream tin at the Marble Bar Tinfields, W.A., and is derived from the degradation of Pre-Cambrian gneiss. The other specimen is a *torbernite* occurring in small flakes adhering to decomposed eruptive rock of intermediate character, and was collected by one of the officers of the Mines Department at the cobalt mine Carcoar (*Records Mines Dept. N.S.W.*, vol. iv., p. 20). The association of cobalt and uranium ores at Joachimsthal in the Bohemian Erzgebirge at Schneeberg, in Germany, and occurrence of slightly radio-active silver cobalt ores at Temiscamingue in Canada has already been remarked by R. W. Brock (*loc. cit.*). This circumstance, however, is regarded by the authors as accidental.

The Australian minerals whose activities have been recorded in the table are with one exception monazites. These *monazites* frequently occur in the tin fields throughout Australia, and on account of their thoria contents have lately become of commercial importance. Monazites are found to a less extent *in situ*, at Torrington in a decomposed granite, and at Warialda embedded in a lode of bismuth carbonate.

New South Wales varieties are of a hyacinth colour, well crystallised, and exhibit two good cleavages. (See *Annual Report Dept. Mines N.S.W.*, 1903; and *Records of Australian Museum*, 1903). The Pilbarra *monazite* in which we have identified the presence of radium (*vide postea*) is darker in colour than the N.S.W. specimens, and cleavages are not so well defined. It is found in the tin wash in association with euxenite and gadolinite. It will be noticed in referring to the figures in the table that no relation can be traced between radio-activity and thoria contents. This points to the presence of some other active substance in addition to the thoria.

The *gadolinite* from the Cooglegong River, W.A., was collected by Mr. B. F. Davis, B.Sc., and is described as

Total Activity as Determined by Ionisation Produced in Air-gap.

Mineral.	Activity.	Locality, &c.
Black oxide of uranium, U_2O_5	100	Taken as standard.
Torbernite	Highly active	Carcoar, N.S.W. (insufficient for comparative test).
Euxenite	Highly active	Marble Bar Tinfields, W.A. (insufficient comp. test).
Gadolinite	0.88	Cooglegong River — Greenbushes Tin-field, W.A.
Monazite	11.30	Pilbarra, W.A.
Fine river sand with gold, tinstone, &c. . . .	8.49	Tumberumba, N. S. Wales.
Zircon sand with monazite	0.60	Tooloon River, N. S. Wales. Contains 0.45 per cent thoria.
Concentrated beach sand	7.39	Broken Head, Richmond River, N.S.W.
Ditto, ditto	1.82	Ballina, Richmond River, N.S.W. 237°
Concentrated river sand..	8.00	Tasmania.
Monazite	5.47	Torrington, N.S.W. A large well developed crystal used.
Ditto	3.25	Torrington, N.S.W.
Ditto	4.92	Cow Flat, Torrington, N.S.W., contains 0.3 per cent thoria.
Ditto	3.11	20 miles W. of Torrington, contains 1.5 per cent thoria.
Ditto	4.46	Ditto, contains 1.8 per cent thoria.
Ditto	3.31	} Various samples from the Gulf Mine, Emma-villa.
Ditto	3.00	
Ditto	3.41	
Ditto	3.13	
Ditto	2.50	Contains 0.6 per cent thoria
Ditto	4.50	Paradise Creek, Emma-ville, N.S.W.

Foreign Minerals.

Pitchblende	354.05	Joachimsthal. } Given for comparison.
Samarskite	47.10	Sweden
Thallium blende	3.75	Locality unknown. Activity may be due to the probable association of uranium minerals.

occurring both with the stream tin in alluvial deposits and in lode formations in Pre-Cambrian gneiss (*Journ. Roy. Soc. N.S. Wales*, 1902, p. 286). In the paper cited an analysis is given, and it is stated that Prof. Norman Collie found 1 bubble of helium in the gases obtained by heating 10 grms. of the mineral. This is the first authentic case in which radio-activity has been noticed in gadolinite.

Examination for Radium.

The method adopted was that used by Hon. R. J. Strutt depending on the decay of the emanation. A preliminary experiment was conducted on 5 grms. of carnotite* from Colorado, U.S.A. Its emanation was found to be strongly active, the rate of decay determining it to be due to radium. Three Australian minerals were next tested with the following results:—

* Since then B. B. Boltwood has published that radium emanation is obtained from this mineral.—*Am. Journ. Sci.*, 1904, xviii., p. 97.

Gadolinite from West Australia (38 grms. tested) gave no radium emanation. In view of the fact that helium is intimately related to radium, this result is extremely interesting, as the gadolinite has been shown to contain helium (*vide antea*). A similar instance is that of a meteorite from Virginia, examined by Strutt (*Proc. Roy. Soc.*, 1904, lxxiii., p. 193). In this case, although the presence of helium was detected by analysis, the meteorite failed to give the radium emanation. In the gadolinite, although thorium is not mentioned in the statement of analysis, later investigation by Acting Professor Schofield showed that a small percentage is present, and the activity is probably referable to this.

Pilbarra monazite (31 grms. tested) gave a definite radium emanation decaying to a half in very slightly under four days. The value of the radium activity cannot yet be assigned until more comparative data are obtainable.

Monazite from Paradise Creek, Emmaville, N.S.W. (25 grms. tested) gave an emanation decaying in a very short time, and not measurable with our apparatus.

Summary.

A number of Australian minerals have been examined for radio-activity by the ionisation produced in an air gap as measured by the most recent form of a C. T. R. Wilson electroscope. The activities are compared with that of black oxide of uranium. Radium was tested for in four of the minerals by heating them in a vacuum, and testing the rate of decay of the radio-activity of the resulting gas.

A gadolinite in which Prof. Norman Collie found helium to be present was radio-active, but no radium emanation could be detected. A number of monazites were radio-active, one from Pilbarra, W.A., gave the radium emanation. It is intended to continue this work shortly, when all results will be published in ampères.

For the suggestion of the research, carried out in the Chemical Laboratory, and for constant encouragement we wish to thank Prof. David. We are indebted to the Department of Mines for a number of minerals, and especially to Mr. G. W. Card, A.R.S.M., for his cordial help in obtaining us specimens. Our thanks are also due to Acting Professors Schofield and Knibbs for encouragement and interest shown in the research.

SOME RESULTS OF LATE MINERAL RESEARCH IN LLANO COUNTY, TEXAS.

By WILLIAM E. HIDDEN.

THE noted gadolinite locality in Llano County, Texas, known as Barringer Hill, was re-opened* and thoroughly prospected by the writer, during the winter of 1902-3, with very encouraging results. All the old cuts were cleaned out and extended, and a systematic development of the mine was begun at the south-east point of the hill, and at as low a level as the river terrace would permit. The plan was to remove the hill by blasting, and gradually make a dump of it towards the near-by Colorado river. The season proved to be a very propitious one, and much good work was accomplished. Seven years had elapsed since any work had been done upon the property, but in a short time all the old familiar minerals had been re-discovered either in new openings or in extensions of the original workings of Mr. Barringer.

Among the most notable discoveries of "Barringer Hill" minerals, at this time, were the double crystal of gadolinite that weighed seventy-three pounds and an eighteen-pound mass of yttrialite; a mass of pure allanite that weighed over three hundred pounds; about fifty pounds of thorogummite, among which were pieces weighing fully a pound and some few good crystals. Of fergusonite several very

pure masses and large aggregations of rough crystals were found, up to five pounds in weight. Of rowlandite one very pure mass weighing just one kilo. was obtained; of nivenite and mackintoshite very little was discovered. The mineral species rich in yttrium-erbium were more particularly sought after because thorium and uranium were not used in the "glower" of the Nernst lamp.

Masses of coarsely crystallised fluorite up to four hundred pounds weight were not rare, and some of these had very large faces of the cube and rhombic dodecahedron. Its colour varied from dark green to puce and purple, and colourless transparent rough crystals having remarkably perfect cleavage were sometimes observed. Some of the fluorite was true chlorophane and exhibited a brilliant green light when strongly heated and viewed in the dark. One mass was self-luminous, at night, without heating it. Enormous crystals of orthoclase were common, some over five feet in diameter. Quite frequently small veins of very perfect red feldspar crystals (highly-twinned), and upon which albite crystals were attached, were found bordering the fluorite and penetrating it. In the feldspar, well crystallised menaccanite was sometimes observed, and this mineral is new to the locality. Yellow rutile, of the sagenitic variety, was observed in only one instance and then upon smoky quartz crystals. Polycrase, or an allied species, was seen implanted upon the gadolinite; this is also new to the region. A cavity into which a horse could have been put was discovered on the river side of the mine, and from it a large crystal of smoky quartz was taken that weighed over six hundred pounds. It was forty-three inches high and twenty-eight inches broad, and fifteen inches thick. This is now in the University of Texas collection at Austin, Texas.

Very fair amethysts were found in the west end of the hill, in cavities in the feldspar. Masses of biotite, four feet across, were met with and always indicated the presence near by of the rare-earth minerals. Some of the fluorite contained small thin veins of a very dark mineral, which was deep indigo-purple by transmitted light, and this may, perhaps, betoken the occurrence of a basic fluoride of the yttrium or cerium earths at this mine and in the region generally.

In a period of four months there was taken out of the hill enough of the yttrium ores to suffice for the Company's needs for the balance of the year, and the mine was therefore closed for the season.

In the following winter (1903-4) the work was again resumed at Barringer Hill, and about a dozen workmen were kept constantly employed for a period of six months. The scheme of development laid down by the writer in 1902 was carried forward with much energy. Considerable "dead-work" was done in the line of removing "topping" and bringing up the "fall" from the river-side of the hill. New cuts were opened, and the whole top of the hill was blasted away. All the work done at the mine thus far has been of the character of open quarry work, with hand-drilling and the use of powder and dynamite. The mine has been proved to have a deep-seated origin and is only one of a series of so-called "blow-outs" in a region that is entirely granitic. Deep work at this locality may be expected to bring to light new combinations of the rare earths and of uranium and of thorium, as well as great quantities of the species for which the hill is already famous. All the old species will probably be found in a purer state and perhaps in their normal condition as when first crystallised. This last mentioned condition is what we are eagerly seeking for in order to clear up the formulæ of many of the species.

During last winter's work all the old minerals, excepting rowlandite, were again found and more than one thousand pounds of very pure gadolinite. The seventy-three pound group of crystals (of gadolinite), found in March, 1903, was the greatest "find" of record in this mineral; but just one year later, a mass of roughly crystallised gadolinite was found, partly imbedded in the bed-rock at the north-east corner of the hill, that measured thirty-six inches long,

* The development was undertaken under the auspices of the Nernst Lamp Company, of Pittsburgh, Pa., to whom all the output was sent.

eleven inches thick at the widest part, and weighed a little over two hundred pounds. It was apparently free from alteration, had specific gravity of 4.28 (taken on a very pure fragment), had a bright green chatoyancy at certain angles, and was like glass in its broad obsidian-like conchoidal fracture.

Upwards of a pound of very pure nivenite and not exceeding an ounce of mackintoshite, were picked out of the many boxes of mixed cyrtolite, fergusonite, and thorogummite. Only the density of nivenite saved it from being thrown away as magnetite (very abundant at this mine), and but for its associations it would be always neglected except by the expert mineralogist. Equally so with the mackintoshite, its resemblance to the dark cyrtolite and intimate association with it, prevents it from being recognised by the miner or layman. Some day this mine promises to be worked for the two last named minerals alone and as the main object of working there, and in the deeper working they should be found abundantly and in a higher state of purity.

Tengcritite (?)—About ten grms. of a white mineral, occurring in semi-globular and flat radiated concretions in the cracks and fissures of the gadolinite, were finally obtained after much labour and search. This quantity was the result of detaching the mineral, bit by bit, from over 300 kilos. of fresh gadolinite. Since the composition of tengcritite (to which species this substance is tentatively referred) is unknown, I submitted the rare mineral to Dr. W. F. Hillebrand, of the U.S. Geol. Survey, for analysis; his report is given in full below. The surprising feature is the presence of glucina (BeO) in the form of carbonate, which is new to science, and this may perhaps indicate a new glucinum mineral mechanically mixed with a basic hydrous carbonate of the rare earths of the yttrium group.

Dr. Hillebrand's Report and Analysis.

"The purest material that could be picked out, from that at my disposal, showed some brown admixture with the white. The following results were obtained from 0.3640 grm. of this selected material, after deducting 0.0262 grm. of residue, left after long treatment of the ignited powder with cold and quite dilute nitric acid.

Y ₂ O ₃ group	40.8 per cent	Mol. wt. ..	226
Ce ₂ O ₃ group	7.0 "	" "	355
Fe ₂ O ₃	4.0 "		
BeO (GIO)	9.7 "		
CO ₂	19.6 "		
H ₂ O above 105° ..	14.1 "		
H ₂ O below 105° ..	3.2 "		
SiO ₂	0.4 "		
MgO, Alk., loss ..	1.2 "		

100.0

All determinations were made on the one portion, the CO₂ and H₂O being directly and simultaneously ascertained by ignition in a tube and collection of the escaping gases. The loss in weight of the ignited powder agreed with the sum of the CO₂ and H₂O found. Approximate molecular weight determinations of the earths, separated into two portions by potassium sulphate, gave 335 for the cerium group and 226 for the yttrium group, the last being the molecular weight of yttria itself. It is certain that some, if not all, of the ferric oxide reported is foreign to the carbonate, but how much it is impossible to say. The calculated ratios lead to nothing definite, except that the white mineral appears to be a hydrous basic carbonate, but whether a double carbonate of the rare earth metals and glucina, or a mixture, there are no present means of deciding."

Radio-activity.—All the minerals of Barringer Hill have been experimented with to ascertain the extent of this form of energy present. As early as September, 1902, the writer was at work upon it, and had then made successful radiographs from specimens mined at this locality as far back as 1889. In the order of their activity, as

shown by their own radiographs, I here mention the species in which the phenomena were observed.

Nivenite (which is a very soluble variety of uraninite) exhibited the most pronounced radio-activity, and beautiful radiographs were made by placing the mineral outside of a photograph plate-holder. Better ones were procured by placing the mineral in direct contact with the sensitive plate—"Cramer's X-ray." Twelve hours exposure, in the dark, developed very good interference figures; but with forty-eight hours, and up to five days exposure, the outlines became as sharp almost as are shown in photographs by sunlight.

Mackintoshite (which is the parent mineral of thorogummite) was next in the amount of radio-activity exhibited. It showed about half the intensity of nivenite when compared with equal exposures of the two minerals, side by side, on the same plate.

Positive evidence of the occurrence, within mackintoshite, of little crystals having even a *higher radio-activity* than that shown by the nivenite, was proven by developing the plates used with direct contact. Little bright spots appeared in the field where the less energetic mackintoshite had touched it, and a dull grey border (made by the thorogummite coating) united to make a radiograph having three degrees of intensity from one mineral specimen. With a strong lens these bright spots, possibly due to a new species, could be identified upon the flattened surface, and they were noticed to be very unlike the surrounding mackintoshite. They resembled galena in colour and in metallic lustre, and were quite evenly distributed over the several flat sections examined. Mackintoshite has given evidence, in thin sections, of being translucent, and of a very dull green colour by transmitted light, but as the purest material yet analysed showed (*vide* Hillebrand's analysis) 4.31 H₂O present, it is possible that these little bright spots are only the normally pure anhydrous mineral. It is tenable also that these little inclusions, with their high radio-activity, are but a normally pure form of nivenite in which only UO₂ is present. Since mackintoshite can be rationally interpreted as being a mixture of three parts of thorite with one of uraninite (nivenite), the assumption that a new mineral has been discovered may not stand. The question is certainly one of unusual interest at this time and merits further investigation.

Thorogummite.—Contact radiographs of this mineral, made from a flattened surface after forty-eight hours exposure, in the dark, had much the appearance of ordinary sunlight photographs. All the minute details of structure and varying degrees of radio-activity were beautifully portrayed. It was surprising to note how perfect a picture this mineral could make of itself without any outside aid other than a photographic plate and a long exposure in the dark.

Masses up to a pound weight were found, and this proves that mackintoshite will not be as rare as it is now, when the mine is worked down to lower levels; for thorogummite is only an alteration product of mackintoshite, it having assumed one more molecule of water and changed its UO₂ to UO₃, and its colour from an apparent jet-black mineral, of specific gravity 5.50, to a dull yellow-brown mineral having specific gravity 4.54+. Long square prisms, like those of zircon, with simple terminal pyramidal planes, were observed.

Yttrialite.—This species gave better radiographs from its altered red crust and its yellow ochreous variety than from the pure dark grey-green anhydrous mineral. All of its radio-activity must emanate from the ten to twelve per cent of thorium present. Hillebrand's last analysis has shown that its composition can best be interpreted by assuming that it is a mixture of an yttrium silicate with the thorite molecule (both anhydrous). Slabs of this mineral eight inches long and six inches broad were broken from some of the larger masses, thus affording fine opportunity for large experimentation in testing it radio-graphically.

Fergusonite.—The mono-hydrated variety made the best

radiographs, but all the varieties (of which there are four at the locality) showed more or less action upon the sensitive film.

A new association was discovered in this species. Symmetrically compounded crystals of nivenite with fergusonite were found in the south walling of the hill. Long square prisms of nivenite with flat terminations had in their centres an equally long but tapering pyramidal crystal of fergusonite, in parallel position. Some of these were one inch long and one-quarter inch thick. The fergusonite was of the purest kind and almost transparent, and somewhat resembled the famous Spanish sphalerite.

Cyrtolite.—Many hundred pounds were found and in great variety of form and colour. All kinds of it gave good radiographs after twenty-four hours exposure. Plates of it as large as one's hand, covered on one side with curved crystals, were not rare. It sometimes encrusted large quartz crystals to the depth of one inch, having radiate structure, and thus afforded a new feature for this mineral and one very uncharacteristic of zircon.

Radial Lines from the Ore Masses.—As early as December of 1902, my attention was attracted to the strange occurrence of unusually long radial lines projecting in many directions from the bodies of ore richest in thorium, uranium, and zirconium. I then named these occurrences "stars," and eagerly sought for them, as positive "pointers" to ore. At last I was obliged to give these "stars" more than passing attention, and here state the reason: While removing, piece by piece, a seventy-pound mass of mixed zirconium-yttrium-uranium and thorium ore, which was a nucleus to one of the best marked of these "stars" from its quartz matrix, my hands and face would begin to burn as if from the effect of strong sunlight, and after two or three days of this kind of mining a redness of skin and a burning sensation would be followed by actual soreness of the parts of my hands and face exposed to the direct emanations from the minerals. My assistant (Mr. J. Edward Turner) complained of it also, and asked me "if these minerals could be poisonous?" As no arsenic was present, the soreness which we both experienced might possibly have been caused by free fluorine, but not by any soluble constituent of the mineral, since salts, such as would be dissolved by the moist skin, had long ago been dissolved, leached out, and re-deposited in the "chimney" of the mine. It was some time after this that the thought came to me that this action might be the work of a radio-active element, and it is offered now more as a suggestion than as a proven fact. I incline strongly to the idea, however, of my having actually experienced the proof of the presence of a very high degree of radio-activity, of a peculiar if not unique kind, at this mine, and that the symptoms above described go a long way towards proving it. Of the true nature of this activity I will not at this time offer any conjectures, but will defer a discussion of it to a paper which is under preparation relating to this very interesting region.

Many photographic records were taken of these "stars;" they are sometimes eight or ten feet across. Although these radial lines are not new to science, having often been noted elsewhere in connection with allanite, monazite, and other rare species, it is not likely that they have been before observed on so large a scale. The cause of this phenomenon has not been determined, so far as I am informed, but it is not without interest that these radial lines are noted only with certain minerals containing rare elements, and are most conspicuous with the radio-active species.—*American Journal of Science*, xix., No. 114.

Microscopic Examination of Metals.—Messrs. R. and J. Beck, 68, Cornhill, have just issued a Catalogue of all the appliances and instruments for the preparation and examination of metals by means of the microscope. As many metallurgists have difficulty in obtaining supplies for this branch of work, our readers may be glad to know that such a catalogue exists and will be sent free on application.

THE USE OF COPPER IN DESTROYING TYPHOID ORGANISMS, AND THE EFFECTS OF COPPER ON MAN.* By HENRY KRAEMER.

It is said that "the life of a Londoner is worth ten to fifteen years' less purchase than that of the average provincial. This fact is due to many causes, but the chief among them is the quality of the water." The same could be said of the residents of many of our American cities. Yet the necessity for a pure-water supply has been recognised since ancient times, and enormous sums of money have and are being spent in the control and purification of water supplies. Our failure to secure pure water has been largely due to ignorance on the one hand, in the past at least, and to mismanagement on the other. It was only in 1873 that Balfour Stewart wrote ("The Conservation of Energy," Chap. I., August, 1873):—

"It is only very recently that we have begun to suspect a large number of our diseases to be caused by organic germs. Now, assuming that we are right in this, it must nevertheless be confessed that our ignorance about these germs is most complete. It is perhaps doubtful whether we ever saw one of these organisms, while it is certain that we are in profound ignorance of their properties and habits. . . . We are at any rate intimately bound up with, and, so to speak, at the mercy of, a world of creatures, of which we know as little as of the inhabitants of the planet Mars.

"Yet, even here, with profound ignorance of the individual, we are not altogether unacquainted with some of the life habits of these powerful predatory communities. Thus we know that cholera is eminently a low level disease, and that during its ravages we ought to pay particular attention to the water we drink. This is a general law of cholera, which is of the more importance to us because we cannot study the habits of the individual organisms that cause the disease.

"Could we but see these, and experiment upon them, we should soon acquire a much more extensive knowledge of their habits, and perhaps find out the means of extirpating the disease, and of preventing its recurrence."

During the past thirty years, since Balfour Stewart wrote these lines, the whole subject of bacteriology has been developed and a distinct science has been created. In many industries bacteriologists are regularly employed to study the problems connected with them and to apply the results so obtained. In those industries which are in the hands of progressive private individuals and corporations, as of brewing, every scientific fact is considered on its merits and utilised if found applicable. On the other hand, the purification of water supplies being, for the most part, in the hands of municipalities, there are many factors which enter into the problem and which render progress very slow. In this connection, however, it is gratifying to note that sufficient progress has been made, in New York City, for instance, to show that the problem is no longer to be considered a political or partisan one. In February of this year the newspapers (*Public Ledger*, February 22, 1905) reported as follows:—

"The spectacle of Mayor McClellan and his old-time rival, ex-Mayor Seth Low, appealing to the State Senate at Albany to-day in favour of the passage of the Mayor's Bill to furnish New York City with a sufficiency of water, is a somewhat moving one. Mayor McClellan's argument in support of his own Bill, according to reports, was no wit less earnest than that of Mr. Low. The non-partisan character of the Mayor's proposal was further attested by the fact that the measure was supported by members of the Low administration."

The problem of the purification of water supplies in the United States, barring for the time being the pollution

* From the *American Journal of Pharmacy*, vol. lxxvii., No. 6.

caused by algæ, may be said to consist essentially of a study of typhoid organisms and of devising measures for their eradication.

The Distribution of Typhoid Organisms.

In the American edition of "Nothnagel's Encyclopedia of Practical Medicine," in the volume on typhoid fever and typhus fever, by Dr. H. Curschmann, edited with additions by William Osler, M.D., on page 38 it is stated:—

"Under the most varied ordinary conditions (not induced experimentally) the typhoid bacillus is capable of surviving for days, weeks, and months, and even for more than a year, and under favourable conditions even throughout the winter. An additional conclusion is permissible, namely that not alone the persistence of the germs, but also their dissemination through the media named, is certain. If in this connection the liquid media in general predominate, the dry media are not to be left out of consideration. It cannot be denied that the contagium attached to particles of dust may be disseminated through the air to a limited degree."

We have, therefore, the highest authority for believing that, contrary to the usual acceptance, the typhoid organism may persist for a considerable period of time, and that infection may occur in very many ways, as through drinking-water, food, and even through the air. In my own experiments I have found that at the ordinary temperature the typhoid bacillus will live over four months in both tap and distilled water, although the organism loses some of its characteristics after two months in that bouillon cultures will not give the agglutinating test with blood of a typhoid patient. (Paper read at the general meeting of the American Philosophical Society, April 13, 1905).

While the isolation of typhoid organisms from water is attended with considerable difficulty, still it has been supposed that when the water supplied a community is free from colon bacilli, it is likewise free from typhoid organisms; that is, the absence of colon bacilli is considered to mean the absence of sewage or fecal organisms. Some recent investigations would seem to indicate that *colon bacilli* are more widely distributed than formerly supposed, and that their presence in water may not always indicate fecal contamination (Erastus G. Smith, "Note on the Occurrence on Grain of Organisms resembling the *Bacillus coli communis*," *Science*, May 5, 1905, xii., No. 530, p. 710). However this may be, the absence of this organism must still be considered one of the best indications of an unpolluted water.

Next to water, milk is considered to be one of the most common sources of typhoid fever; but where the matter has been investigated it has been found that the milk was contaminated with water containing sewage organisms. Chapin, in his book on "Municipal Sanitation in the United States," page 511, cites an instance of this kind in the tracing of an epidemic of typhoid fever in Springfield, Mass., some years ago. He says:—

"The contents of the privy were spread on a lot near the well, and the men walked over this in going to the well, and their boots were rinsed off on the planking over the well and the water below. In this water *Bacillus coli* was found. The cans of milk were cooled in this well and it was found that the water leaked into the cans. Another chance for contamination was directly from the infected hands of convalescents."

Oysters and shell-fish taken from beds near where sewage is discharged have also been found to be a source of the disease.

Recently it has been shown by Dr. Benjamin Lee (Editorial comment in *Amer. Medicine*, November 26, 1904, p. 906), of the Pennsylvania State Board of Health, that water-cress may collect a sufficient amount of extraneous organic matter containing colon bacilli to be a source of infection.

While it is usually conceded that typhoid organisms are chiefly disseminated through water and milk, yet the free

use which is made of privy manure or night-soil in some localities as a fertiliser on truck farms renders it probable that fecal bacteria, including typhoid, are disseminated through the use of garden vegetables. In many instances this manure is allowed to stand in large pools, and by means of dippers is sprinkled over the soil. In August, during the heavy rains, I have seen low plants like lettuce and spinach completely washed with this more or less dilute liquid manure.

The experiments of Dr. Lee show how difficult it is to wash out the organisms from cress, and the same would apply to vegetables like lettuce and celery, in the latter case the soil being sometimes heaped up around the plants to prepare them for the market. No doubt in many instances certain fruits which are eaten in a raw condition, as tomatoes, apples, pears, &c., are sources of infection.

In a recent paper Dr. Barringer (*The Virginia Medical Semi-Monthly*, February 12, 1904, p. 501) gives a number of observations which tend to show that the dust from American railroad beds, through the discharge of typhoid patients while travelling over the roads when in the infective stage, is a probable source of typhoid infection, which has not been generally appreciated.

The Removal or Destruction of Typhoid Organisms in Food and Water.

Heretofore there have been two principal methods for the removal of typhoid organisms from drinking water, namely: (1) Filtration on a large scale, and (2) filtration and boiling on a small scale. Many bio-chemical methods for the purification of water have been proposed, some of which may be enumerated:—

1. Aqua regia followed by sodium carbonate.
2. Bleaching-powder followed by sodium bicarbonate.
3. Various permanganates, as potassium, calcium, aluminum, or barium.
4. Perchloric acid.
5. Bromine followed by ammonia.
6. Iron chloride and sodium carbonate.
7. Sodium bisulphate.
8. Peroxide of chlorine.
9. Kerosene.
10. Silver salts.
11. The alum process has been used for purifying the water supplies of large cities.

The use of electricity (12), as also of ozone (13) has been proposed.

The use of copper (14) for the purification of water on a large scale was first proposed by Dr. Moore and Mr. Kellerman, in a Bulletin of the U.S. Department of Agriculture a year ago. In a second Bulletin issued some weeks ago the authors have confirmed the efficiency of copper in the purification of water contaminated by algæ. They also report in one instance the abatement of an epidemic of typhoid fever in New Mexico, after treatment of the water-supply with copper sulphate. At Columbus, O., the water was treated with copper sulphate during September, October, November, and December, when the number of typhoid cases was reduced to from four to sixteen per month. The treatment was discontinued and the number of typhoid cases rose from 91 to 376 per month during January, February, and March.

That copper has a marked toxic or oligodynamic action on fecal bacteria, including typhoid bacilli, has been known since the experiments of Israel and Klingmann (*Virchow's Archiv*, 1897, cxlvii., pp. 293-340) were reported in 1897, and their observations have been confirmed by Moore and Kellerman and by every one who has worked along these lines since. (See papers by M. E. Pennington, N. Gildersleeve, and A. H. Stewart in *American Journal of Medical Sciences*, May, 1905; and by W. P. Mason, *Science*, April 28, 1905). I have found that when copper foil is allowed to remain in distilled water from one to five minutes sufficient copper is dissolved by the water to kill typhoid organisms within two hours.

The Effects of Copper on Lower Animals and Plants.

It is well known that the action of copper salts upon both plants and animals varies quite considerably. Seeds, for example, may be treated with quite concentrated solutions of copper sulphate without impairing their germinating activities. I have sprayed certain plants, as the common plantain and poison ivy, with ten per cent copper sulphate solutions without noticing any ill effects. Very many plants withstand spraying with solutions of copper sulphate containing as much as 1 part per 1000. The effects vary greatly according to the conditions which surround the plant. Seedlings of pea and corn, for instance, are killed when placed in solutions of copper sulphate 1 part to 200,000; but when the seedlings are placed in soil containing 1 part or even more of copper sulphate in 2000 parts of soil they remain uninjured.

Nägeli's experiments, performed during the '80's, showed that certain unicellular plants, as the algae, were killed by solutions containing exceedingly minute quantities of copper ("Ueber oligodynamische Erscheinungen in lebenden Zellen," *Neue Denkschriften der schweizerischen naturforschenden Gesellschaft*, xxxiii.-xxxiv., 1893-1895). His experiments have been repeatedly confirmed, and Israel and Klingmann observed a similar toxic action on other unicellular plants, notably some of the fecal bacteria and also on some of the unicellular animal organisms.

While there are these experiments showing that certain plants and animals are killed by solutions containing as little as one part of copper to 1,000,000,000 of water, still there are other plants which are stimulated and under certain conditions even appear to be benefitted by its presence. Frank and Kruger (*Ber. d. Deutsch. Bot. Ges.*, 1894, xii., p. 8) have shown that if potato plants are properly supplied with copper, the plants are harder, yield a larger crop, and live longer than they otherwise would.

We may say in a general way that there are certain organisms which manifest a specific sensitiveness towards copper, including bacteria, one of the annelid worms, as well as other human parasites, while others are unaffected or even stimulated by relatively large quantities of copper sulphate. The unicellular organisms are the ones which appear to be most sensitive to the action of copper.

(To be continued).

BIBLIOGRAPHICAL NOTES ON TANTALUM
AND THE OCCURRENCE OF TANTALUM IN
FRANCE.

THE following may be looked upon as the principal papers published on the application of tantalum to incandescent electric lamps.

M. Von Bolton, chemist to Messrs. Siemens and Halske, and M. Feuerlein, engineer to the same firm, have described their researches extending over several years, in a paper read before the *Electrotechnischen Verein* of Berlin, on January 17, 1905, and their communications were published by the *Electrotechnische Zeitschrift* of January 26.

M. Banville gave the *Société Internationale des Electriciens* at its meeting in May, a paper on incandescent lamps, in which he referred particularly to those of tantalum. Finally, M. Bolton has also published his researches in the *Zeitschrift für Elektrochemie* of January 20.

The success of the tantalum lamp should draw attention to the sources of this rare and precious metal. It is not met with frequently in France. According to the recent work of Schilling, the following are the deposits or minerals in which it is found; a few others ought to be added, such as that of Beauvoir, which has been acquired by Messrs. Siemens and Halske.

Tantalite.—Is met with at Chantelaube near Limoges. It contains 82.98 per cent of tantalum, with iron, tin, manganese, and silica, according to the analysis made by

M. Damour (*Comptes Rendus*, vol. xxv., p. 670). Other samples from the same locality contained 78.98 per cent of tantalum, with zirconium, tin, iron, and manganese, according to the analysis made by Jenzsch (*Poggendorfer Annalen*, vol. xcvii., p. 107); and 79.89 per cent of tantalum, with tin, manganese, iron, calcium, and copper, according to Chaudler and Rose (*Poggendorfer Annalen*, vol. civ., p. 100.)

Tungsten Ochre.—Is found at Meymac, in Correze; it contains from 1.1 to 5.0 per cent of tantalum, according to the analysis of Carnot (*Comptes Rendus*, vol. lxxix., p. 637).

Neotantalite.—Is found in the mines of zinc and kaolin at Colettes and Echassières in Allier; it contains from 22 to 23.1 per cent of niobium, and from 57.7 to 60.58 per cent of tantalum, with iron, manganese, tin, potassium, sodium, lithium, silicon, aluminium, calcium, magnesium, and uranium, according to the analysis of Pisani and Ternier (*Zeits. für Krist. Min.*, vol. xxxix., p. 183; *Bull. Soc. Trans.*, vol. xxv., pp. 34-38).—*Bull. Soc. d'Encouragement pour l'Industrie Nationale*, June 30, 1905, p. 800.

CHEMICAL NOTICES FROM FOREIGN
SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxl., No. 26, June 26, 1905.

Hydrolysis of very Concentrated Solutions of Ferric Sulphate.—A. Recoura.—The author finds that a very concentrated solution of ferric sulphate in a well-corked flask spontaneously decomposes into a solid basic sulphate of well defined composition, $6[\text{Fe}_2\text{O}_3, 3\text{SO}_3] \cdot \text{Fe}_2\text{O}_3 \cdot \text{Aq}$, which is only slightly soluble and of a yellowish white colour, and also a soluble acid sulphate or a mixture of neutral sulphate and free acid. This decomposition is not instantaneous; it is a function of the time. The rapidity and amount of the decomposition are greatly influenced by different circumstances which the author investigates.

Compounds of Aluminium Chloride and Carbon Oxychloride.—E. Baud.—When carbon oxychloride is liquefied over anhydrous aluminium chloride, this salt entirely dissolves, and if it is then left to itself at ordinary temperatures for the excess of gas to be evolved, a colourless liquid product remains, which solidifies at -2° , and has for its composition (1) $\text{Al}_2\text{Cl}_6, 5\text{COCl}_2$. The author also proves the existence of the two further compounds, (2) $\text{Al}_2\text{Cl}_6, 3\text{COCl}_2$, (3) $2\text{Al}_2\text{Cl}_6, \text{COCl}_2$. The compound (2) corresponds to the neutral carbonate, $\text{Al}_2\text{O}_3, 3\text{CO}_2$, which has not hitherto been isolated. The last compound is present in commercial aluminium chloride. Finally, the solution of aluminium chloride in liquid carbon oxychloride will probably be able to effect syntheses which were not possible with solid aluminium chloride.

Constitution and Properties of Tin Steels, Titanium Steels, and Cobalt Steels.—Léon Guillet.—The author's researches on tin, titanium, and cobalt steels show that these metals enter into solution with the iron, and that the carbon of these steels is, at least within the author's experimental limits, in a state of iron carbide. The mechanical properties of these steels show them to be of practically no commercial importance, but prove clearly the very sharp difference existing between tin, titanium, and silicon steels, on the one hand, and nickel and cobalt steels on the other.

Hydrogenation of the Aldoximes.—A. Mailhe.—The hydrogenation of the oximes can be easily effected by MM. Sabatier and Senderens' method of using finely divided nickel and hydrogen. Operating at a temperature between 180° and 220° the first product obtained is a

primary amine containing the same amount of carbon as the oxime, and produced according to the reaction $RC=NOH.R'+2H_2+H_2O+RCH.NH_3.R'$. At the temperature of the reaction, however, the nickel decomposes the primary amine according to the equation:—
 $\frac{2R}{2R'} > CH.NH_2 = NH_3 + \left(\frac{R}{R'} > CH\right)_2NH$.

Bromuration of Paraldehyde.—P. Freundler.—The bromuration of paraldehyde at a low temperature causes the production of bromoacetic aldehyde. This becomes crotonised above 0° in presence of hydrobromic acid, but the crotonisation is limited. In presence of an excess of bromine the dibromocrotonic aldehyde is transformed into tetrabromobutyric aldehyde, an inert and very stable substance, but whose chain is broken when placed in contact with hydrobromic acid. The complex $CH_2Br.CBr=CBr.CHO$ being very unstable.

Some New β -Ketoaldehydes.—F. Couturier and G. Vignon.—The authors prepare a number of new β -ketoaldehydes by Claisen's method modified by the use of metallic sodium on a mixture of formic ether and the particular ketone. The sodium salt of the ketoaldehyde formed when dissolved in ice-water, acidulated by acetic acid, and treated with copper acetate carefully freed from basic acetate, gives the copper salt of the ketoaldehyde, which can be purified by washing with petrol ether and crystallisations from ether. By this method the following compounds were prepared:—Diethylacetylaldehyde, $C_2H_5 > CH-CO-CH=CHOH$; trimethylacetylaldehyde, $C_2H_5 > CH-CO-CH=CHOH$; isovalerylaldehyde, $(CH_3)_3C-CO-CH=CH.OH$; isobutylacetylaldehyde, $CH_3 > CH-CH_2-CO-CH=CHOH$; isobutylacetylaldehyde, $CH_3 > CH-CH_2-CH_2-CO-CH=CHOH$.

Monomethylamine Iodomercurates and Chloroiodomercurate.—Maurice François.—The author prepares monomethylamine iodomercurates and monomethylamine chloroiodomercurate from monomethylamine by the action of mercuric iodide.

Derivatives of Butyrolin and Capronin.—L. Bouveault and René Locquin.—The authors investigate the properties and prepare a number of derivatives of butyrolin and capronin.

A Bivalent Phytosterine-alcohol.—T. Klobb.

The Combustion of Sulphur in the Calorimetric Bomb.—H. Giran.—The heat of formation of sulphurous anhydride from its elements in M. Berthelot's calorimetric bomb apparently increases with the pressure. The author supposes this increase to be due to the formation of persulphuric anhydride, which should increase with the pressure. To prove this hypothesis, he measures the heat of formation of S_2O_7 from SO_3 and O .

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxviii., No. 6, 1905.

Complex Compounds of Pentavalent Vanadium with Tetravalent Elements.—Wilhelm Prandtl.—By warming a solution of selenious acid with vanadium pentoxide, yellowish-red crystals (double refracting) are obtained, which are difficultly soluble in water. Their composition corresponds to the formula I. $3V_2O_5 \cdot 4SeO_2 \cdot 4H_2O + 6aq.$ or II. $3V_2O_5 \cdot 4SeO_2 \cdot 4H_2O + 10aq.$, the former being obtained from solutions containing excess of selenious acid, or on evaporating the vanadium selenious acid with hydrochloric acid, while the latter is prepared from exactly equal parts by weight of vanadium pentoxide and selenium dioxide. On dissolving the vanadium selenious acid in alkalis, alkali vanadium selenites are obtained, and of these two series may be prepared, the salts being red or yellow according to the proportions of V_2O_5 and SeO_2 used in their preparation. Neither series has the same type of formula as the free acid. The salts are prepared

by boiling definite quantities of vanadium pentoxide and selenium dioxide with water for a few minutes, adding the hydroxide and water till a clear, colourless, feebly alkaline solution is obtained. This is then acidulated with acetic acid, filtered, and allowed to crystallise. The salts which have been prepared thus are (red) ammonium vanadium selenite, (red) potassium vanadium selenite, (yellow) ammonium vanadium selenite from solutions containing excess of selenium dioxide, and yellow potassium vanadium selenite. The sodium and lithium salts being very readily soluble have not yet been prepared pure.

Action of Silent Electric Discharge upon Chlorine.—Franz Russ.—Using a high tension current obtained from the secondary coil of a large inductor provided with a Wehnelt interrupter, the author found that chlorine, when exposed to a silent electric discharge, suffers a decided change. The action of chlorine thus treated upon benzene was investigated, and it was found that:—1. By the simultaneous action of a silent electric discharge and light upon chlorine, active chlorine is prepared. 2. By the action of either light alone or the electric discharge alone only a very slight degree of activity is produced. A far greater quantity of active chlorine is obtained by the simultaneous action of these two factors. 3. The degree of activity depends upon the magnitude of the dielectric and upon the dryness of the chlorine. If the gas is led through water before being allowed to act upon the benzene it loses almost all its activity. 4. The chlorine retains its activity at ordinary temperatures even when led through tubes of considerable length, e.g., 200 c.m. Three experiments showed that the amount of benzyl chloride formed was the same as when the benzene was immediately behind the discharge vessel. 5. The activity is lost when the gas is heated. 6. The question whether the joint action of light and a silent electric discharge produces a new modification of chlorine analogous to ozone, or whether the activity is due to the formation of intermediate products, has not yet been decided. 7. When quartz vessels are substituted for glass, five and a-half to six and a-half times as much benzyl chloride is formed as in glass vessels under similar conditions. This is to be explained by the fact that quartz is far more transparent to ultra-violet rays than glass, and evidently most of the effect of daylight upon a mixture of chlorine and benzene is due to the ultra-violet part of the spectrum. The use of a quartz mercury lamp for illumination has the same effect.

Triphenylmethyl.—M. Gomberg and L. H. Cone.—Triphenylmethyl forms molecular compounds with esters, a large number of these compounds having been prepared and investigated. Their composition seems to be ex-

pressed probably by the formula
$$\begin{array}{c} R.C \equiv O \\ \diagup \quad \diagdown \\ R' \quad O \quad C(C_6H_5)_3 \\ \diagdown \quad \diagup \\ R' \quad O \quad C(C_6H_5)_3 \end{array}$$
 and thus one of the oxygen atoms has become tetravalent. Triphenylmethyl also forms compounds with the aromatic and unsaturated aliphatic hydrocarbons, and with a constituent of petroleum ether. All these addition products exhibit the characteristic reactions of triphenylmethyl, forming the peroxide, $(C_6H_5)_3C.O.O.C(C_6H_5)_3$, on addition of oxygen.

Mercuric Fulminate.—Lothar Wöhler and K. Theodorovits.—When nitric acid containing no oxides of nitrogen is employed in the preparation of mercury fulminate by the usual method the reaction is only very feeble, and small quantities of metallic mercury are formed. The same holds good when lignone is substituted for alcohol. Acetaldehyde acts upon an ice-cold solution of mercury in concentrated nitric acid, the reaction taking place instantaneously and white fulminate being formed. Dimethyl acetal also acts in the same way, but not so vigorously. As aldehyde is an oxidation product of alcohol it was to be expected that the process would be simpler with acetal than with alcohol, and simplest with aldehyde, and this was found to be the case. The action with alcohol is by far the least energetic, and the product

is always coloured grey or yellowish brown, owing to the presence of metallic mercury. Methyl alcohol gives no fulminate, nor do propyl alcohol, aldehyde, acetone, and methyl ketone in the ordinary way. Thus it appears that a di-carbon chain is necessary for the formation of the fulminate, and that no fulminate is formed unless the methyl group is present in the alcohol, acetals, aldehyde, and its polymers. The CH_3 group, moreover, must be combined with CH_2OH , or $\text{CH}=\text{O}$, or $\text{C}\equiv\text{O}$, or $\text{C}=\text{H}$; CH_3CN , for example, only reacts feebly, and no fulminate is formed.

Palladium.—C. Paal and Conrad Amberger.—The authors find that the reduction of palladium salts by means of hydrazine sulphate, both in acid and alkaline solution, leads to the formation of elementary palladium. They explain this contradiction of Jannasch and Bettges' results by supposing that these authors had either confused their preparations with the oxygenated preparations which had been ignited in air, or else that the hydrogen used for the reduction acted in presence of the oxygen of the air, when finely divided palladium would act catalytically (like platinum), forming water, even in the cold. When performing these experiments the authors always expelled the air by means of carbon dioxide before allowing hydrogen to act upon their preparations.

Solid Solutions of Indifferent Gases in Uranium Oxides.—V. Kohlschütter and K. Vogdt.—The authors studied the compound of uranic acid and hydroxylamine with a view to discovering in what condition helium is present in uranium minerals. They found that on heating uranic acid hydroxylamine to 125° a slow intramolecular decomposition of the hydroxylamine takes place, N_2 , N_2O , NH_3 , and H_2O being formed. The ammonia and water escape, but the nitrogen and nitrous oxide remain practically quantitatively dissolved in the uranic acid. Apparently they form a perfectly homogeneous mixture with it, from which they escape when the substance is dissolved in acids. On heating *in vacuo* the preparation still retains the gases up to about 300° , and apparently the uranium oxide only possesses the power of dissolving the indifferent gases as long as it contains a definite amount of water. From experiments with cleveite the authors are persuaded that only minerals with a certain amount of water in them contain any appreciable quantity of helium.

MISCELLANEOUS.

British Pharmaceutical Conference.—The forty-second annual meeting of this body was opened at the Hotel Metropole, Brighton, on Tuesday, July 25th. This is an organisation distinct from the Pharmaceutical Society, and is solely concerned in "the encouragement of pharmaceutical research, and the promotion of friendly intercourse and union amongst pharmacists," whereas the Pharmaceutical Society is a statutory body charged with the administration of the Pharmacy Acts, and the examination and registration of those who desire to be registered under these Acts. The Conference was received by the Mayor and Mayoress at the Royal Pavilion on Monday evening, and on Tuesday morning the President, Mr. W. A. H. Naylor, F.I.C., F.C.S., of London, delivered an address. Thereafter satisfactory reports of the position of the Conference were submitted, and the reading and discussion of communications resulting from researches was commenced. It was attended by nearly 300 pharmacists from all parts of the United Kingdom, and several Colonial chemists are amongst the number.

International Congress for the Study of Radiology and Ionisation, Liège, 1905.—The first International Congress for the Study of Radiology and Ionisation will be held during the present year at Liège, between the 12th

and 14th of September (inclusive). The Congress will be divided into two sections:—**Physical Section.**—I. The Physics of Electrons, including radiations of various kinds. II. Radio-activity and Dependent Transformations: The activity of waters and earths; Radio-active deposits. (The above outlines of the work to be considered as suggestive rather than limiting. The programme is intended in fact to include the study of all questions having to do with radio-activity). III. Meteorological and Astronomical Phenomena and their relation to ionisation and radio-activity. **Biological Section.**—The programme governing the work of this section will include an examination of the physiological properties of various radiations and of radio-activity, and will consider their medical value and application. The method of procedure in this section will be determined upon by a special commission presided over by Professors Bouchard and d'Arsonval, members of the Institut de France, and of the Academy of Medicine of Paris. Beside this special commission, a general committee, composed of men notable for research work in matters of interest to this investigation, and presided over by M. Henri Becquerel, will examine, classify, and approve such reports, papers, and notes as may be offered. Intending contributors are requested to forward the manuscript of their papers at their earliest convenience, and the titles immediately if possible.

The Evolution of Oxygen observed during the Decomposition of Cupric Metaborate.—W. Guertler.—On evaporating a solution containing one molecule of nitrate of copper and 2 molecules of boric acid, and heating the residue without exceeding a temperature of 950° , we obtain blue crystals of the metaborate $\text{B}_2\text{O}_3\text{Cu}$. These crystals are doubly refracting, $D=3.859$; they are unattacked by dilute mineral acids, and have the hardness of corundum. When fused they form a black glass more easily attacked than the crystals, having a density of 3.61. The same metaborate is obtained more easily by the fusion of the nitrate with an excess of acid. After fusion we obtain two layers, the upper one of which forms a greenish glass soluble in water, and the lower one consists of blue crystals of the metaborate. If we raise the temperature to about 1000° , we obtain an abundant evolution of oxygen. Even at a lower temperature, by sufficiently prolonging the heating, we observe the formation of a red amorphous mass. The metaborate fuses at about 970° ; this constant, however, is difficult to determine, as the evolution of oxygen commences at about 875° . The loss of oxygen is about 5.3 per cent, and results from the decomposition of the metaborate according to the equation:— $6\text{B}_2\text{O}_3\text{Cu} = 3\text{Cu}_2\text{O} \cdot 2\text{B}_2\text{O}_3 + 3\text{O} + 4\text{B}_2\text{O}_3$. The new borate thus formed, $3\text{Cu}_2\text{O} \cdot 2\text{B}_2\text{O}_3$, can be easily isolated by taking up the product of decomposition with water. It occurs as brown crystals having a greenish colouration on the surface. The author has not been able to reproduce this substance by the direct action of boric acid on protoxide of copper.—*Zeit. Anorg. Chem.*, vol. xxxviii., p. 456.

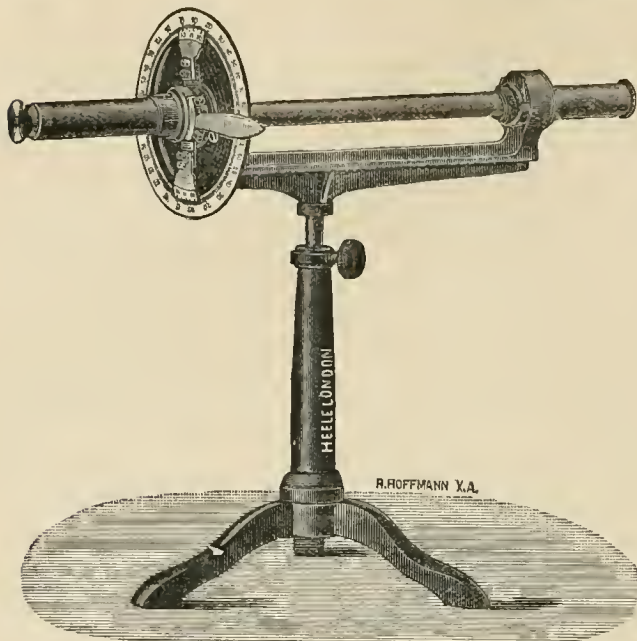
ST. PAUL'S SCHOOL, West Kensington.—

An EXAMINATION will be held at the above School on Tuesday, September 5th, 1904, and on the following days, for filling up about Twenty Vacancies on the Foundation.—Full particulars of the Examination can be obtained on application to the Bursar.

TO BE SOLD, the English Patent referring to Apparatuses for Wood Impregnation (mining) applicable to Tar Distillation and Founding, &c. Thirty-six installations have been started in Germany, with large profits.—For particulars address, in German, "K.D. 3573," Rudolf Moase, Cologne.

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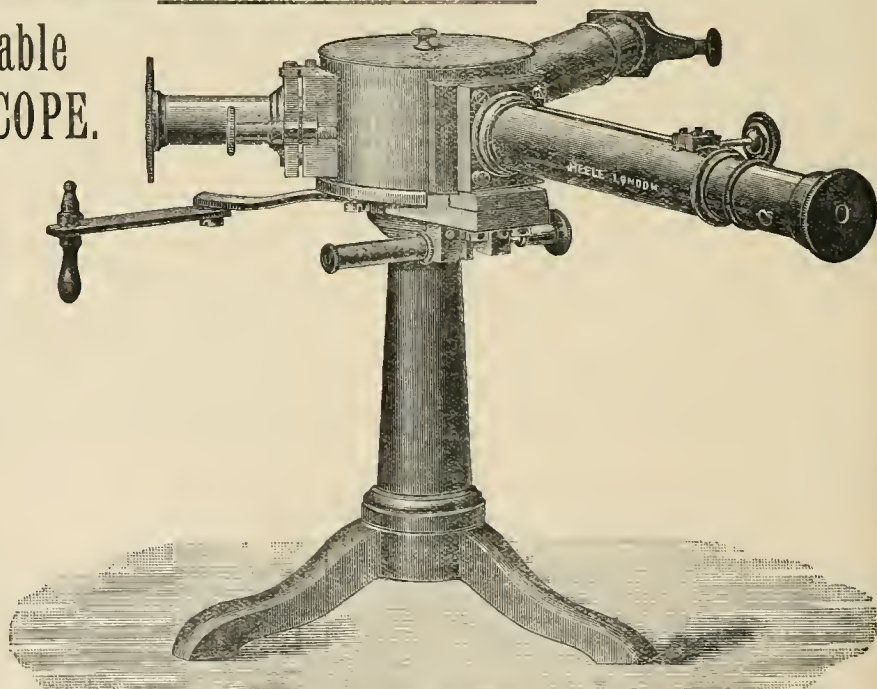
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THE CHEMICAL NEWS.

VOL. XCII., No. 2384.

THE PERCOLATION OF RAIN-WATER THROUGH SOILS.

By W. F. SUTHERST, Ph.D., F.R.C.

THE continued drought in the North and Midlands has naturally dried up the soil to a considerable extent; so much, indeed, that certain light soils are practically sun-dried to the depth of several inches, leaving the roots of the various crops growing in them more or less out of reach of any moisture. To see how much rain it actually needed to moisten the dried soil up to certain depths, a series of experiments was carried out here on various classes of soils.

A tube $1\frac{1}{2}$ inches in diameter was taken and filled with sun-dried specimens of soils and pressed down so as to resemble as near as possible their condition in nature. On these were placed from time to time portions of water equivalent to 0.1 inch and multiples of the same (2.5 c.c.). From this were noted—(1) The depth to which the water extended; (2) the time to reach this depth; and (3) the time the water remained on the surface of the soil before finally disappearing. The following tables give the figures obtained by these experiments:—

I.—Sandy Loam.

Inches of rain.	Depth. Inches.	Time.		Time on surface.	
		Mins.	Secs.	Mins.	Secs.
0.1	$\frac{1}{2}$	0	15	0	0
0.2	$1\frac{1}{2}$	0	40	0	1
0.3	$1\frac{1}{2}$	0	40	0	1
0.4	$1\frac{1}{2}$	0	45	0	2
0.5	$1\frac{1}{2}$	0	50	0	2
0.6	$2\frac{1}{2}$	1	0	0	2 $\frac{1}{2}$
0.7	$2\frac{1}{2}$	1	15	0	2 $\frac{1}{2}$
0.8	$2\frac{1}{2}$	1	20	0	2 $\frac{1}{2}$
0.9	$3\frac{1}{2}$	1	30	0	3
1.0	$3\frac{1}{2}$	1	35	0	3

II.—Loam.

0.1	$\frac{3}{4}$	0	20	0	2
0.2	$1\frac{1}{2}$	0	50	0	6
0.3	$1\frac{1}{2}$	1	30	0	12
0.4	$1\frac{1}{2}$	2	0	0	23
0.5	$1\frac{1}{2}$	3	0	0	35
0.6	$2\frac{1}{2}$	4	0	1	0
0.7	$2\frac{1}{2}$	5	15	1	30
0.8	$2\frac{1}{2}$	6	35	2	50
0.9	$3\frac{1}{2}$	7	50	4	0
1.0	$3\frac{1}{2}$	9	20	5	20

III.—Clay Loam.

0.1	$\frac{1}{4}$	0	50	0	20
0.2	$\frac{1}{2}$	2	30	1	15
0.3	$\frac{3}{4}$	4	0	2	0
0.4	$1\frac{1}{4}$	6	15	2	30
0.5	$1\frac{1}{2}$	8	0	3	0
0.6	$1\frac{1}{2}$	10	15	4	0
0.7	$2\frac{1}{4}$	14	10	4	45
0.8	$2\frac{1}{2}$	20	30	5	20
0.9	$2\frac{1}{2}$	27	15	6	35
1.0	$2\frac{1}{2}$	35	10	8	0

IV.—Heavy Clay Soil.

		Hours.	Mins.		
0.1	$\frac{3}{4}$	0	4	2	30
0.2	$1\frac{1}{2}$	1	0	20	0
0.3	$1\frac{1}{2}$	2	50	45	0
0.4	$1\frac{1}{2}$	4	0	60	0
0.5	$1\frac{1}{2}$	7	0	90	0

V.—Garden Soil.

		Mins.	Secs.		
0.1	$\frac{1}{2}$	0	40	0	5
0.2	$\frac{1}{2}$	0	50	0	8
0.3	$1\frac{1}{2}$	1	5	0	10
0.4	$1\frac{1}{2}$	1	20	0	15
0.5	$1\frac{1}{2}$	1	40	0	19
0.6	$1\frac{1}{2}$	1	55	0	23
0.7	$2\frac{1}{2}$	2	20	0	28
0.8	$2\frac{1}{2}$	2	50	0	33
0.9	$2\frac{1}{2}$	3	20	0	40
1.0	$2\frac{1}{2}$	3	55	0	46

Experiments carried out some years ago by Lawes and Gilbert demonstrated that over 50 per cent of the rainfall is evaporated before it has the chance of percolating through the soil, so that really it would need more than twice the rainfall to penetrate the depths obtained by the above trials. As, however, the rain remains for such a long period on clay soils before percolating, it stands to reason that in these cases much more than 50 per cent of it must disappear by evaporation and draining from the surface, the latter more so in case of sloping lands.

The Agricultural College, Tamworth.

THE DECAY CONSTANT OF THE EMANATIONS OF EMANIUM AND ACTINIUM.

By O. HAHN and O. SACKUR.

THE decay constant of the emanation of Giesel's emanium has not yet been determined; its numerical value is of special interest in reference to the question whether emanium, as has often been suggested, is identical with Debiere's actinium. According to Giesel's qualitative statements, emanium emanation loses its activity after a few seconds.

We used for our measurements a preparation kindly placed at our disposal by Giesel. This was wrapped in paper, and placed in the front part of a glass tube filled with wadding; air was then blown over it into the measuring tube. The experimental arrangement was exactly similar to that employed in the experiments with radium emanation carried out by one of us (*Berichte*, 1905, xxxviii., 1753). A few seconds after the emanation had been blown in, the earth connection of the pair of quadrants connected with the measuring tube was removed. The electrometer needle was deflected, but its rapidity became visibly less. After about half a minute the rapidity, and thus the conductivity, in the tube had become constant. In order to be able to establish the time this decrease of rapidity takes, we marked by pencil strokes the position of the image of the needle upon the scale after equal periods of time marked by the beats of a metronome (e.g., 1.3 sec.).

The calculation of the duration of life of the emanation from these measurements may be performed as follows:—The experiment gives us the distance of the needle from the zero-point as a function of the time. As special experiments showed, with the electrometer used the deflection of the needle is proportional to its potential v . Hence, we at once obtained its increase with the time, i.e., the function $v = f(t)$.

The increase of the potential dv in time dt is caused by the electricity passing through the interior of the measuring tube. This is proportional to the conductivity, and thus to the activity, of the emanation and to the induced activity produced on the walls. If we denote the former by i_1 and the latter by i_2 , then $\frac{dv}{dt} = i_1 + i_2$. According

to the known exponential law, $i_1 = i_0 e^{-\lambda t}$.

i_2 also decreases according to an exponential law, but so slowly that it may be regarded as constant during the few seconds the measurement takes.

Therefore $\frac{dv}{dt} = i_0 e^{-\lambda t} + i_2$, and, after integration,—

$$v = i_0 \int e^{-\lambda t} dt + i_2 t = -\frac{i_0}{\lambda} e^{-\lambda t} + i_2 t + C.$$

If $t=0$, $v=0$, and $C = -\frac{i_0}{\lambda}$; hence $v = \frac{i_0}{\lambda} (1 - e^{-\lambda t}) + i_2 t$.

After less than half a minute, as mentioned above, the rapidity of the deflection of the needle is constant, and thus is only determined by the magnitude i_2 , the induced activity; thus, i_2 is given by the experiment. Hence the value of $i_2 t$ can be calculated for each period of time, and can be deduced from the measured deflection v . In this way we obtain a corrected function, $v' = \frac{i_0}{\lambda} (1 - e^{-\lambda t})$,

which expresses only the increase of potential caused by the activity of the emanation itself. This equation is transcendental as regards the decay constant λ , and cannot be solved for λ . But the following consideration leads to its calculation.

After a sufficiently long time (less than half a minute), as experience shows, v' becomes constant, and the needle would remain still if it were not driven forward with the rapidity corresponding to the induced activity. This

maximum value of v' is $v'(\text{max.}) = \frac{i_0}{\lambda}$. It has been directly determined experimentally on many occasions, and on others, in which it would lie outside the scale employed, it can be determined accurately enough graphically by extrapolation.

Moreover, $\frac{v'}{v'(\text{max.})} = 1 - e^{-\lambda t}$, and therefore—

$$\lambda = \frac{1}{t} \log_e \frac{v'(\text{max.}) - v'}{v'(\text{max.})}.$$

The following method of calculation is simpler:—The value $\frac{v'}{v'(\text{max.})}$ is equal to $\frac{1}{2}$ if $e^{-\lambda t} = \frac{1}{2}$, i.e., in that time in which the activity of the emanation has sunk to half its value. Thus we obtain the so-called "half-period of life" as that period of time after which the deflection of the needle has reached half its maximum value, and this can be interpolated with great accuracy from the curves obtained empirically. The following example makes this method of calculation clearer:—

Time. Secs.	v . Scale divisions.
1.2	60
2.4	115
3.6	160
4.8	200
6.0	230
7.2	258
8.4	277
9.6	293
10.8	311
12.0	325

The constant residual activity amounted to 6 scale divisions in 1.2 seconds. Thus the following values are calculated:—

v' corr.	v' corr.
54	222
103	235
142	245
176	257
200	265

Extrapolation gives $v'(\text{max.}) = 290$. The half value 145 is reached after 3.7 seconds. After this time, therefore, the activity of the emanation has sunk to half its value. Three other series of experiments with the same preparation

gave the values 3.8, 3.3, and 3.3 secs., and three series with another preparation, which Giesel called emanum X, gave the values 3.6, 3.6, and 3.3 secs. The mean of all seven series is 3.6 secs. The absolute value of the decay constant λ is therefore $\frac{\log_e 2}{3.6} = 0.19$.

Exactly the same measurements were carried out with an actinium preparation kindly given us by Debiegne. For the time in which the intensity of the emanation sinks to half its value we obtained the numbers 3.8, 3.9, and 4.0 secs. Thus the mean value was 3.9 secs., and the decay constant λ therefore equals 0.21. This agrees perfectly with the number given by Debiegne, and the difference between it and the number obtained for emanum lies within the limits of experimental errors.

Contradictory statements are to be found concerning the time of decay of the induced activity resulting from emanum and actinium emanations. Debiegne gives for actinium about 40 mins. (*Comptes Rendus*, 1904, cxxxviii., 411), and Miss Brooks the same for emanum (*Phil. Mag.*, 1904, [6], viii., 373). Giesel, on the other hand, from the measurements of Elster and Geitel, gives 34.4 mins. (*Berichte*, 1904, xxxvii., 3963), and Bronson 36 mins. (*Amer. Journ. Sci.*, 1905, [4], xix., 185). Hence we considered a new determination desirable.

We found the following method applicable for the production of a strong induced activity:—The emanation was led for several hours through a glass spiral, which was cooled by liquid air. The emanation condensed in this, and was transformed into induced activity. After stopping the current of gas the tube was washed out with warm hydrochloric acid, and the latter was evaporated to dryness in a little dish. The decrease of activity can be followed by measuring the rapidity of discharge of an electroscope. By this method we obtained for the induced activity produced by Debiegne's actinium the following times of decay to the half value:—36.0, 36.2, 36.2, 37.0, 37.2 mins., the mean value being 36.5 mins., and the corresponding values for Giesel's emanum were 36.3, 36.3, 36.5 mins.; but it must be confessed that single series of experiments with both preparations led to somewhat higher values up to 40 mins. for some unexplained reason.

In any case it has been proved by our measurements that Debiegne's actinium and Giesel's emanum produce the same emanation and the same induced activity. They are thus probably to be regarded as identical.

We are greatly indebted to Giesel and Debiegne for sending their preparations, and to Sir William Ramsay for the trouble he has taken.—*Berichte*, 1905, xxxviii., 1943.

TANTALUM AND ITS ALLOYS.

Much interest has recently been shown by engineers, metallurgists, and others in the new uses to which the metal tantalum has been applied, particularly in the alloys of tantalum with steel. Messrs. Siemens, Halske, and Co., of Askanischer Platz, Berlin, have just had granted to them a British patent for tantalum alloys, which are more particularly for use for bearings, cams, eccentrics, rollers, and those portions of machinery subject to great wear. They claim that their tantalum alloys with carbon and steel can be made almost as hard as a diamond.

The following information is extracted from Messrs. Siemens, Halske, and Co.'s specification:—

Tantalum possesses, like steel, the property of being easily worked and hardened; it has also great resistance to fracture and great elasticity. Its hardness can be increased to such an extent as to greatly exceed that of the best kinds of steel and that of the stones usually employed. As regards the greatest degree of hardness which it can attain, it is almost equal to the diamond. It has the further advantage over steel in being one of the precious

metals which is not affected by the atmosphere, and which, at ordinary temperatures, completely resists the action of most acids. In the case of mechanisms of precision this property is of the greatest importance. In order to be able to work the metal satisfactorily, it must be previously well fused. By the fusing process it is at the same time freed from impurities and brought to a state of a homogeneous body. The fusing is effected best *in vacuo*, and by means of the electric current.

The metal which has been melted can be readily worked mechanically in any known manner; it can be hammered, rolled, drawn, filed, and the like, and can thereby be wrought into every desired form. When being mechanically worked, the metal, in particular when it contains a small quantity of carbon or other hardening medium, readily assumes so great a degree of hardness that the further working is rendered impossible, and it must then be carefully re-heated or annealed in order to be again rendered soft. In this annealing process care must be taken that the temperature does not rise too high, as otherwise the material is more easily attacked by the oxygen of the atmosphere. The metal will, however, even in the form of the finest drawn wires or thinnest rolled bands, stand a heating in the open air, up to a dark red heat, without being appreciably affected. When so heated the metal shows a colouration similar to tempered steel. In order to prevent too great a heating, in particular of minute parts of metallic tantalum, it is preferable to effect the heating indirectly by raising large plates or drums to the temperature to which the parts to be heated are required to be brought, and then to bring the objects made of tantalum to be heated in contact with these plates or drums. If, on the other hand, it is desired to raise the objects made of tantalum to higher temperatures, without being materially affected on their surface, it is of advantage to effect the heating *in vacuo*, as at very high temperatures metallic tantalum combines with almost all known substances. The heating *in vacuo* is preferably effected by electrical means, such as by the use of electrical resistances or directly by passing an electric current through the objects to be heated. For imparting great hardness to the metallic tantalum other substances can be added thereto; in particular carbon serves for this purpose, which acts upon metallic tantalum in the same way as it does upon steel. But numerous other substances, such as oxygen, hydrogen, silicon, boron, aluminium, titanium, and tin can be used. When using carbon as the hardening medium the tantalum becomes very hard and resisting, even with the presence of a small fractional part of 1 per cent. Also, of the other above-named substances, only very small quantities are required in order to produce great hardness. If the mixture of such hardening substances is increased materially above the small proportions mentioned, the metallic tantalum generally becomes so brittle that no further working of the same is possible. The extent of the permissible quantity of carbon or other substances must be determined in each separate case according to the particular conditions and character of the substances chosen.

A subsequent hardening of already worked parts of soft metal can also be effected by heating the metal to redness in carbon, in a similar manner to the treatment of steel.

As metallic tantalum is at present very expensive, only those parts will, of course, be made of tantalum that are directly subject to strong mechanical action, such as the linings of bearings, the cones and balls for the ball bearings of machines and mechanisms, and the like. For many purposes also in place of pure metallic tantalum, alloys of the same can be used which exhibit good properties—for example, alloys of tantalum with iron. The most serviceable alloys of iron are, on the one hand, those which consist of iron containing only small quantities, up to a few parts per cent of tantalum, or which consist of tantalum having only a few parts per cent of iron. The properties of these alloys can be varied to a very great extent by varying the proportions of the constituents.—*The Times Engineering Supplement*, July 26, 1905.

NOTES ON HEAT INSULATION, PARTICULARLY WITH REGARD TO MATERIALS USED IN FURNACE CONSTRUCTION.*

By R. S. HUTTON and J. R. BEARD.

Introduction.

THE importance of a knowledge of the heat conductivity of the materials used for the bricks or linings of furnaces scarcely needs to be emphasised. There is no doubt that a careful study of this subject would enable a very large saving to be effected in the fuel or other heating costs in many experimental and industrial furnaces.

The manufacturer and purchaser of refractory products both seem to ignore the necessity for accurately determining the quality of their material so far as its heat insulating power is concerned. Their specifications are confined to other properties, but it is doubtful if any of them are of greater economic importance than the heat conductivity.

So far as laboratory crucible and muffle furnaces are concerned, H. H. Cunyngame (*Journal Society of Arts*, Dec. 11, 1903, vol. lii., p. 72; also *Engineering*, Dec. 11, 1903) has recently shown how greatly the efficiency can be improved by the adoption of better insulation.

Despite this lack of knowledge the measurement of thermal conductivities of such materials is by no means difficult to carry out, at any rate to within an accuracy of 2 or 3 per cent. C. H. Lees and J. D. Chorlton (*Phil. Mag.*, June, 1896, [5], vol. xli., pp. 495-503) have specially designed a simple apparatus for measuring the thermal insulation of bad conductors. We are much indebted to Dr. Lees, who very kindly lent the apparatus, and also gave much valuable advice in carrying out the experiments.

Measurement of Thermal Conductivities of Granular Materials up to 100° C.

All the substances dealt with have been either in the state of well-defined granular powders, or in some few cases where bricks have been examined, these were previously broken up and finely powdered. The apparatus of Lees and Chorlton was originally designed for round tiles or plates of material, but these have to be of uniform thickness and 11.4 c.m. diameter, and the shaping of bricks is not easily accomplished in the laboratory. A sketch of the apparatus is given in Fig. 1. It consists essentially of two thick metal discs between which the material is placed whose thermal conductivity has to be measured. The upper disc is surmounted with a steam jacket, whilst the lower one is allowed to cool by free conduction and radiation. Three thermometers are used, one to give the temperature of the upper, the second that of the lower disc; whilst a third gives the temperature of the surrounding air. The thermometers are inserted into radial holes drilled in the discs and thus denote their temperature with fair accuracy. When steam is passed through the steam jacket the temperature of the upper disc is raised to nearly 100° C., heat flows through the material experimented on, and thus raises the temperature of the lower disc above that of the surrounding air. The lower disc loses heat by conduction and radiation to the air. Eventually a steady state is reached, when this loss of heat is equal to the heat received through the material experimented on.

The following equation enables the thermal conductivity (K) to be calculated from the result of such an experiment provided h_1 , the external conductivity or "emissivity," has been previously determined:—

$$K = \frac{t_2 - t_1}{t_3 - t_2} \cdot b \left(h_1 + h_1' + \frac{\rho h_1}{2q} \cdot b \right);$$

where t_1 , t_2 , and t_3 are the temperatures indicated by the thermometers T_1 , T_2 , and T_3 respectively, and b denotes the thickness of the layer of powder.

The value of h_1 is determined in a separate experiment

* Read before the Faraday Society, July 3, 1905.

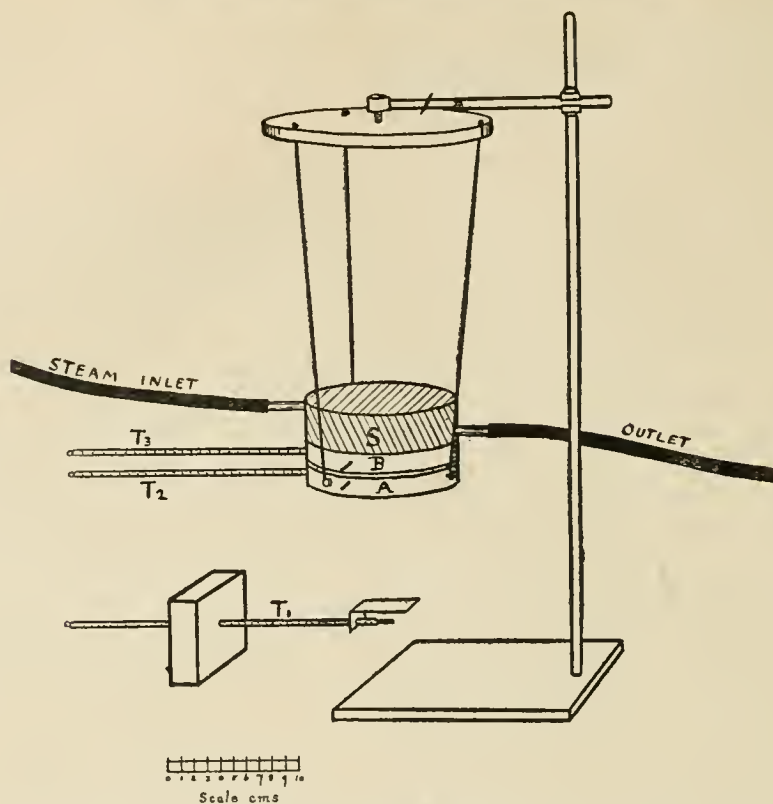


FIG. 1.—APPARATUS OF LEES AND CHORLTON FOR MEASUREMENT OF THERMAL CONDUCTIVITY OF BAD CONDUCTORS.

A=Round disc of brass on which the substance under investigation is placed; it is suspended from a horizontal support by three strings. The disc is 11.4 c.m. diameter and 1.3 c.m. thick. The powders are kept in position by a thin ring of red fibre, which in the present work was about 0.36 c.m. high.

B=Upper disc of brass of same dimensions as A. It is surmounted by the steam box s, which is covered with felt to diminish the loss of heat.

A and B are provided with projecting pegs, the distance apart of which gives a measure of the thickness of insulating material.

T_1 is a thermometer registering the temperature of the air; it is provided with a screen to protect it from radiated heat from the lower disc.

T_2 and T_3 indicate the temperature of the lower and upper disc respectively, they are inserted into radial holes drilled in the brass.

from the rate of cooling of the lower disc at different temperatures.

In all the experiments here recorded the thickness was practically the same (0.360 c.m.), and as in nearly all cases the thermal conductivities were much of the same order, the term in the bracket was very nearly constant and equal to 0.00046.

Substance.*	Thickness in c.m.	Temperatures, °C			Conductivity. K.
		t_3	t_2	t_1	
Sand. White Calais ..	0.360	98.4	81.0	18.2	0.00060
Carborundum (fine) ..	0.363	98.7	78.8	18.3	0.00050
Carborundum (coarse) ..	0.358	98.7	79.6	18.7	0.00051
Quartz "Enamel" ..	0.362	99.3	75.4	21.7	0.00036
Quartz (fused) ..	0.362	98.9	74.9	17.4	0.00039
Firebrick ..	0.363	98.7	69.2	20.3	0.00028
Retort graphite ..	0.363	100.0	76.6	19.6	0.00040
Lime ..	0.363	98.1	70.1	20.8	0.00029
Magnesia (fused) ..	0.356	98.7	78.6	20.0	0.00047
Magnesia, "Mabor" brick	0.360	99.7	80.0	18.8	0.00050
Magnesia, calcined Greek	0.365	99.3	78.3	20.4	0.00045
Magnesia, calcined "Veitsch" ..	0.366	99.7	73.9	20.0	0.00034
Magnesia, Pattinson's light calcined ..	0.363	98.0	58.5	19.7	0.00016
Kieselguhr (infusorial earth)	0.366	97.9	53.9	17.7	0.00013

* Most of these granular powders just passed through a sieve with 600 meshes per sq. c.m.

Relative Value of different Heat Insulating Materials at High Temperatures.

It is not advisable to choose a material suitable for furnace uses from the above data alone.

Firstly, it is always necessary to know the general effect upon the substance under investigation of such temperatures as are likely to be experienced. Several, even amongst those materials mentioned in the table, are unsuitable for subjecting to high temperature on account of the physical changes, such as shrinkage, which they undergo. Chemical action, especially oxidation, also renders many insulators unsuitable for a large number of purposes.

Secondly, having by such considerations excluded all unsuitable materials from the choice, it becomes necessary to compare the relative efficiency of those which remain under conditions more nearly approaching those experienced in practice.

The following experiments were carried out with a view to testing in as simple a manner as possible the behaviour of various refractory materials at comparatively high temperatures.

The method employed, although it does not directly lend itself to the accurate measurement of the absolute conductivities, at any rate offers a practical means for making comparative tests.

Description of Apparatus.

A modified form of electrically heated tube furnace was

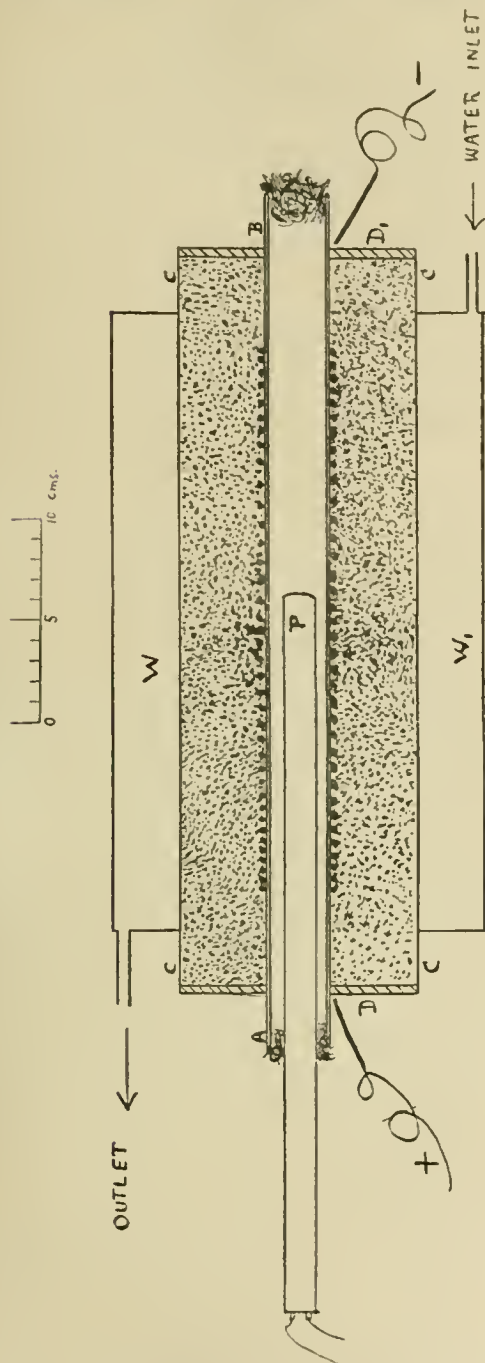


FIG. 2.—APPARATUS USED FOR COMPARISON OF HEAT INSULATORS AT HIGH TEMPERATURES.

A, B, Unglazed porcelain tube with heating coil of nickel wire wound on its central portion.
 The porcelain tube is kept in position at the centre of the cylinder of sheet iron, C, C, C₁, by washers of asbestos card, D, D₁.
 W, W₁ is the water jacket surrounding the cylinder C.
 P is a thermo-electric pyrometer by which the temperature is indicated.
 The granular insulating material under test fills the space between the porcelain tube and sheet-iron cylinder.

employed. An unglazed porcelain tube, with a heating coil of nickel wire, is supported at the centre of a cylindrical, water-cooled enclosure, the space between the heating coil and the inner wall of the enclosure being filled with the granular material under investigation. (See Fig. 2.) The electric energy expended in the wire is kept constant over a considerable period by careful adjustment of an external resistance and constant observation of a precision wattmeter. The temperature at the centre of the porcelain tube is noted at regular intervals, and from the observations a curve is plotted to show the relation between the rise of temperature and the time during which the heating has been in progress. The temperature of the water flowing through the external jacket was kept fairly constant; generally it varied some 2° C.

In such an experiment it would require a very long time for the temperature to attain a constant value. It was therefore found preferable, after the rate of increase in temperature had become rather slow, to reduce the power by a small but definite amount. Under these conditions the temperature falls, at first very rapidly, but soon reaches a constant value, or at any rate falls so slowly as to be almost negligible. It is from a comparison of the heating curves with different materials and the same expenditure of power, and particularly from the nearly horizontal portion of the curves with lower power expenditure, that valuable conclusions can be drawn.

The accompanying diagram (Fig. 3) illustrates some of the results obtained.

In the case of firebrick, carborundum, and sand, the preliminary heating was effected with 300 watts, and after the lapse of about two hours the power was reduced to 250 watts, being kept constant at this for a period of one and a-half to two hours, by which time the temperature had become almost constant. The curves for kieselgur (infusorial earth) and light magnesia clearly show the very much smaller conductivity of these materials. (cf. F. A. J. FitzGerald, *Electrochemical Industry*, 1905, vol. iii., p. 55).

With these two substances the preliminary heating was effected with an expenditure of only 150 watts, but despite this the rise in temperature is more rapid than with any of the other materials mentioned.

Unfortunately, neither light magnesia nor infusorial earth can withstand any high temperatures for long without losing their efficiency to a considerable extent. Both substances exhibit large shrinkage at high temperature, and their chief uses are likely to be limited to external jacketing of furnaces lined with some more permanent but less good insulator.

To more thoroughly test the above method of comparing the relative efficiency of different materials at high temperatures, it was thought advisable to see what influence the preliminary heating might have on the results.

Two similar experiments were therefore carried out with the various substances. In the first case the preliminary stage of the heating was effected with 300 watts, in the second with 250 watts. In both cases the power was subsequently reduced to 200 watts, and then to 150. The results showed that in all those cases in which no permanent alteration is brought about in the materials under test, the horizontal portions of the curve are practically identical, whatever the preliminary treatment had been.

In earlier experiments, in which no water-cooling had been used to maintain constant the temperature of the outer jacket of the enclosure, some anomalous results were obtained.

General Conclusions.

The above results will, it is hoped, prove of value to those who have to deal with refractory materials. The subject seems to have been much neglected, considering that the thermal conductivity of such substances is the characteristic property which is really applied in their many uses.

Whilst bricks and generally jacketing materials for furnaces should be of low thermal conductivity, it is of no less importance to choose crucibles, retorts, and other con-

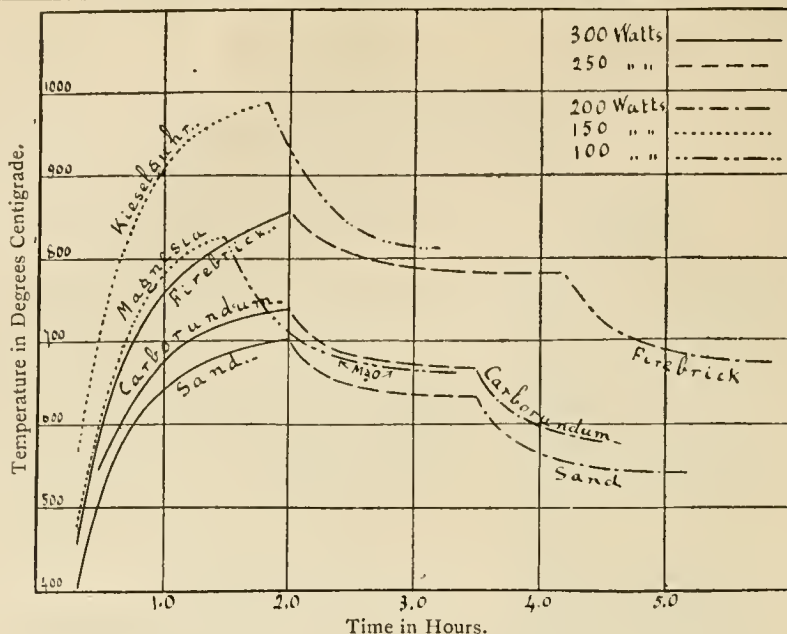


FIG. 3.—CURVES SHOWING RELATIVE INSULATING POWER OF MATERIALS.

taining vessels which are heated externally of as high conductivity as is feasible in conjunction with their other necessary qualities. Such methods as have been described are equally applicable to this latter case.

By a judicious use of the different materials and a stratified form of construction, it should be possible usefully to employ such excellent insulators as infusorial earth without risk of the damage which is inevitable if they be permanently subjected to too high a temperature.

The above experiments were carried out in the Physical Laboratories of the Manchester University.

THE USE OF COPPER IN DESTROYING TYPHOID ORGANISMS, AND THE EFFECTS OF COPPER ON MAN.*

By HENRY KRAEMER.

(Concluded from p. 45).

The Effects of Water Treated with Copper on Man.

WHILE it has been conclusively shown that exceedingly minute quantities of copper are toxic to typhoid organisms, still the question is raised by some as to the toxic effects on man when copper or its salts is used in the purification of drinking-water. In commenting on a paper of mine on "The Efficiency of Copper Foil in Destroying Typhoid and Colon Bacilli in Water," a reviewer writes as follows (*Medical Notes and Queries*, March, 1905, i., No. 3, p. 38):—"While recommending the use of copper foil for the purification of drinking-water, the writer adduces no proofs as to freedom from toxic effects when water so purified is taken into the system over a considerable period of time." My reason for not taking up the pharmacological phase of this question heretofore has been that my own experiments in the consumption of water treated with copper foil did not extend over a sufficient period of time to warrant me in making any statements in regard to the effects of water so treated. Then, too, I felt that the statements of pharmacologists and physiologists were con-

clusive as to the probable harmlessness to man of copper when used in the proportions necessary to purify water containing typhoid organisms. But since there seems to be some objection in certain communities to the drinking of water treated with copper, I have deemed it advisable to give my own experience in connection with this subject.

For over six months all of the drinking-water consumed in my home has been treated with copper. A strip of copper foil, or sheet copper, 9 inches square, is placed in a vessel containing from 3 to 4 quarts of water and allowed to remain from four to eight hours. The foil is first cleaned with powdered pumice, and retains its lustre for weeks unless the water contains a considerable quantity of sediment, and provided the quantity of water is renewed immediately each time upon drawing off the sterilised water. On account of the varying amounts of sediment we find it desirable to filter the water before treating it with the copper foil. Up to this time no ill effects have been noted from drinking the water so treated, and, in fact, our general health may perhaps be said to be better than usual, in that we have not had to consult a physician during this time. Another interesting observation is that the water being more palatable than boiled water, we consume larger quantities, which possibly has some influence on the general bodily condition.

Believing, as I have already indicated, that many vegetables may also be a source of infection, we take the precaution either to wash the vegetables to be eaten raw in copper-treated water, or to place them, particularly in the case of lettuce and celery, in a vessel of water along with a strip of clean copper foil and allow them to remain from two to four hours with occasional agitation.

The use of copper vessels would be more convenient, but of course is more expensive. I have also thought that water-pitchers and tumblers might be partly lined with pieces of copper foil.

I may say in addition that I know of a number of families who have been using copper-treated water for even a longer period of time without any untoward effects.

The Elimination of Copper from Water.

Nägeli (*loc. cit.*) discovered during the course of his experiments that a solution of copper that was toxic to

* From the *American Journal of Pharmacy*, vol. lxxvii., No. 6.

Spirogyra could be rendered harmless by the introduction of a number of more or less insoluble substances. Among those which he used for this purpose were the following: Sulphur (either roll or flowers), carbon (either graphite or soot), coke, coal, peat, black oxide of manganese, starch, cellulose (either as Swedish filter-paper, or cotton, linen, or wood fibre), silk, wool, stearic acid, paraffin, gum, dextrin, egg albumin, glue. True and Oglevee (*Botanical Gazette*, 1905, xxxix., pp. 1-21) have studied the influence of insoluble substances on the toxic action of poisons in solution, and have not only confirmed Nägeli's observation, but have shown that sand and powdered glass have the property of reducing the toxicity of solutions of copper. Moore and Kellerman have shown in their recent Bulletin the relative decrease of the toxicity of copper sulphate solutions according to the amount of organic matter present, the amount of carbon dioxide dissolved in the water, or the temporary hardness of the water.

In addition, the copper is absorbed by the organisms which are killed, and is thus eliminated. It is therefore apparent that there are a number of ways by which the copper is removed from solution and the toxicity of solutions containing it lessened.

In the case of reservoirs treated with copper it is likely that none or very little copper remains in solution for any considerable period of time. By a combination of factors, such as (a) absorption by the organisms that are killed as well as by other organic matter; (b) by the formation of insoluble compounds with various inorganic salts; and (c) by adsorption by various insoluble materials, the copper is removed, so that by the time the water reaches the consumer there is probably no copper in solution, and the insoluble copper, if present, is necessarily more or less inert. Furthermore, I am of the opinion that there is more copper in solution in home-filtered water which has been treated with copper foil than in the water which reaches the consumer after treatment of a large reservoir with copper sulphate in the quantities proposed by Moore and Kellerman for the purpose.

The Occurrence of Copper in Foods.

Among the other inorganic constituents which occur normally in the animal organism is copper, and its occurrence is so constant as to be spoken of as "normal copper." It is not known, however, what part, if any, it plays in metabolism. The amount normally present varies with the food and with the individual. There is considerable data showing that the amount of copper in vegetables varies according to the amount of copper present in the soil, and owing to its wide distribution in soil, it is found in many plants. It is therefore naturally present in many foods, and may run as high as 0.560 gm. per kilogram. of dried substance, or even 1 part in 1785 parts, in plants growing near copper works, as shown by Lehmann (*"Hygienische Studien über Kupfer IV."*, *Arch. f. Hygiene*, 1896, xxvii.).

In addition, copper is added to many foods to enhance their appearance. The custom of greening vegetables has been followed in a commercial way for over fifty years, and laws are being enacted defining the limit of copper which is permissible in food materials. The Swiss and Italian Governments allow a quantity of metallic copper not to exceed 100 m.grms. per kilogram. (or 1 part in 10,000) in vegetable preserves. In France the question of re-greening vegetables by means of copper sulphate has received careful attention, and while the practice was prohibited by law in 1853, this prohibitory law was repealed in 1889. According to Leach:—"Examination of a large number of brands of canned vegetables greened by copper, as bought in Massachusetts, showed that the amount varied from a trace to 2.75 grms. per can, calculated as copper sulphate. . . . In the Massachusetts market labels like the following are not uncommon: 'This package of French vegetables contains an equivalent of metallic copper not exceeding three-fourths of a grain.'" In Pennsylvania the law "permits articles of vegetable

food to contain as much as $\frac{1}{10}$ of 1 per cent of metallic copper," or 1 part to 5000 parts of food.

The Effects of Foods containing Copper on Man.

Being without any other reliable data as to the physiological effects of copper on man, save as a medicine, we naturally turn to the foods containing copper for evidence as to the effects of copper on man. The question has been repeatedly discussed before the courts, particularly in England, and the studies of Lehmann and others in Germany have contributed materially to an elucidation of the problem.

It is probable that the copper naturally occurring in plants is in a condition different from that found in food products which have been artificially treated with copper. That is, in the former case the copper is in a labile condition, and therefore more assimilable, while in the latter case the compounds formed by the combination of the copper with the proteids and chlorophyll are less soluble, and the copper is extracted only in part by acids of the strength of the gastric juice. According to Tschirch and Brandel (quoted by Dr. Smith in Buck's "Handbook of Medical Sciences"), the copper in these more or less insoluble compounds is but slightly toxic. "From experiments with copper proteid Filehne concluded that an amount equivalent to 0.500 gm. of copper per day would produce no notable result in an adult" (Buck's "Handbook of Medical Sciences").

"Contrary to the earlier teachings, recent observations tend to the view that there is no chronic copper poisoning comparable with that of lead. According to this view the long continued ingestion of minute doses of copper by the stomach and the exposure to absorption in handling and working the metal, are not capable of producing systemic poisoning. This view is based largely upon the negative results obtained in feeding experiments with man and the lower animals, and in the therapeutic use of copper salts" (*loc. cit.*).

Galipe had all of the foods which were used in his family for fourteen months cooked in copper vessels, and reported that no trouble was experienced. Dr. Smith (*loc. cit.*), in discussing the use of copper utensils for cooking purposes, says:—"It seems impossible that enough copper could be present in food which would be eaten at one time to produce serious acute poisoning as has been frequently supposed, especially as the presence of as much as $\frac{1}{4}$ a gm. of copper in 1 kilogram. of liquid food would produce a marked metallic taste."

Pasteur says (*Ann. d'Hyg.*, publ. Par., Series 3, iii., p. 204, March, 1880):—"In regard to the toxicity of copper salts, it may be said it is almost impossible to take a dose large enough to produce death, both from their horrible taste and from the violent vomiting which they produce. In small quantities the taste is not perceptible, and the salts are not only tolerated but absorbed. Workers in copper are often completely saturated with the metal, but do not suffer from it. Experiments on animal and human subjects have never given a worse result than vomiting or a temporary fit of colic. Copper normally exists in the human body. It gains entrance from various foods and drinks in the absence of all adulteration. It accumulates to a certain extent, but injury from this accumulation is unknown. In the sample submitted, copper exists to an extent varying between 16 and 45 m.grms. per kilogram. . . . The quantity found does not constitute a danger to health."

Conclusions.

1. It is pretty well established that the typhoid organism is disseminated not only through water, but also through air and food, and may retain its vitality for a considerable period of time.

2. Typhoid organisms in water are eliminated by filtration, boiling, and certain biochemical methods. Of the latter, the use of copper, as proposed by Moore and

Kellermann, is probably the most efficient and at the same time most practicable.

3. While exceedingly minute quantities of copper in solution are toxic to certain unicellular organisms, as bacteria, it is safe to assume that the higher plants and animals, including man, are unaffected by solutions containing the same or even larger amounts of copper.

4. There being a number of factors which tend to eliminate copper from its solutions, it is hardly likely that there would be any copper in solution by the time the water from a reservoir reached the consumer if the treatment of the reservoir were in competent hands.

5. Many plants contain relatively large quantities of copper, and when these are used as food some of the copper is taken up by the animal organism, but there are no records of any ill effects from copper so consumed.

ZINC DUST.

By A. B. STEVENS.

BEFORE using zinc dust in some experiments upon the gum obtained from Japanese lac I wished to be sure that it was free from nitrogen; I therefore subjected the zinc dust to the following tests, the results of which may be of interest to those who frequently use it in connection with organic substances.

When heated with potassium hydroxide it formed ammonia. When heated alone it also gave off ammonia. This led to the belief that nitrogen in some form had been absorbed from the atmosphere, and might be removed by heat. A small quantity was therefore placed in a loosely covered crucible, and strongly heated for half an hour. When cold it was tested for nitrogen by heating with potassium hydroxide. Its vapours rapidly changed litmus-paper from red to blue. Upon the suggestion of Professor Tschirch a sample was thoroughly washed with water acidulated with hydrochloric acid, but this failed to completely remove the nitrogen.

As zinc dust is manufactured by heating zinc oxide with coal, it was believed that part of the nitrogen might consist of condensation products from the coal. Therefore a sample was placed in a long tube and percolated with ether. The ether when evaporated left a yellow, non-saponifiable oil, with an odour and fluorescence similar to petroleum. The oil, when heated with dry potassium hydroxide, gave off alkaline vapours, and the zinc in the percolator was still found to contain nitrogen. The greater portion of the oil appeared to be removed with the first portion of ether, but after continued percolation the ether left a residue upon evaporation, and it was evident that a much larger amount of ether was necessary for complete exhaustion; therefore a smaller sample, from a can of zinc dust which had been in the laboratory for more than ten years, was treated with ether in the same manner, and the powder tested from time to time. After using a large amount of ether the zinc was practically free from nitrogen, yet by taking a large amount of the zinc and heating with potassium hydroxide in a tube partially closed at the top so that all of the vapours came in contact with the litmus-paper, the colour was slightly changed, thus showing a mere trace of nitrogen. This sample was then allowed to stand in an open flask for a few days, when it gave a decided ammonia reaction, thus showing that zinc dust rapidly absorbs nitrogen from the air.

The fact that only a portion of the nitrogen in zinc dust is removed by heat indicates that the nitrogen is present in more than one form. This theory is also supported by the following experiments:—

A fresh sample of zinc dust was washed with water, the washings giving a decided ammonia test. The washing was continued as long as traces of nitrogen could be detected in the washings. It was then treated in the same manner with very dilute hydrochloric acid. By adding

potassium hydroxide in excess to the acid solution and allowing to stand a few minutes until the precipitate settled, decanting the clear solution and boiling, the vapours gave the odour of ammonia and rapidly changed litmus from red to blue. Washing with acid was continued until the washings no longer gave a test for nitrogen. The zinc was then washed with water until free from acid, and rapidly dried in a drying oven, and at once extracted with ether, the ether evaporated and tested for nitrogen as above. Nitrogen was found to be present, though not in as large amounts as in the oil from the first sample examined, which was, however, directly treated with ether.

Three samples were examined: one from a large closely covered can which has been in use in the laboratory as above stated; another from a glass bottle which has been in the museum about fifteen years, and a third which was ordered by Professor Oesterle for these experiments. Practically the only difference found in the three samples was that the oil from the fresh sample was decidedly yellow, while that from the laboratory sample was somewhat lighter, and that from the museum sample was colourless.

Dr. V. Steger ("Metallimpfe in Zinkhütten," "Chem. und Chemischtechnischer Vorträge") gives the results of several analyses of zinc dust, some of which contain considerable insoluble residue consisting principally of carbon. To determine to what extent this was present, a large amount of zinc dust was treated with hydrochloric acid. At first the reaction was rapid, but after a time ceased. The solution was decanted and fresh acid added, but as the reaction was very weak the mixture was heated. Even then a large amount remained undissolved. A few drops of copper sulphate solution were added and digested for several days, but a large amount remained insoluble. This was washed with water until free from acid, dried, and percolated with ether, which upon evaporation left a colourless oil. Upon removing the ether the zinc dissolved without difficulty in hydrochloric acid, conclusively proving that this sample contained no carbon, and that the insolubility was due to the presence of the oil.—*American Journal of Pharmacy*, lxxvii., No. 6.

NOTICES OF BOOKS

Twenty-ninth Annual Report of His Majesty's Inspectors of Explosives: being their Report for the Year 1904. London: Darling and Son, Ltd., 1905. Pp. 241.

DURING the year 1904 there have been two modifications of the law, viz., Order of Secretary of State, No. 4 (a), regulating the deposit of explosives in dust-bins, &c., for conveyance as rubbish, and Order of Secretary of State, No. 7, consolidating and re-arranging the regulations in regard to the packing of explosives for conveyance.

We are glad to note that the Inspectors have found no reason to complain of any falling off in the general conditions of factories and magazines, and that they have not had occasion during the year to institute legal proceedings for any irregularity brought to light by their inspections. The occupiers of factories and magazines have invariably shown perfect readiness to remedy such defects as have been pointed out, and the managers themselves, in many instances, have introduced improvements tending towards greater safety.

The number of deaths from accidents by fire or explosion in the manufacture of explosives is considerably above the average for the past ten years, viz., 13, compared with 7.5. Still this number of deaths is not excessive, and will compare favourably with the death-rate in other dangerous trades.

The total number of factories under continuing certificate or license is 148, being an increase of 1 during the year; of the above total, 4 factories are under notice of temporary disuse.

During the year there have been 19 explosives added to the authorised list, and 17 added to the authorisable list.

It will be seen on reference to Dr. Dupré's report, Table I., that out of 417 samples examined by him 66 were rejected.

During the year, 241 visits to factories have been made; the number of accidents occurring during this period is 42, causing 13 deaths, and injuring 29 persons, but it is as well to point out that a considerable proportion of the total number consists of accidents of an unimportant character, while in the case of some of the accidents by which persons were injured the injury was slight.

Several cases of the illegal manufacture of blasting cartridges by miners in their houses were brought to light by accidents during the year, and three other cases of the manufacture of unauthorised explosives were found.

The number of magazines under continuing certificate and license is now 425, being an increase of 5 on the previous year, and it is satisfactory to find that there has been no case of accident by fire or explosion in connection with any magazine during 1904.

The amount of foreign blasting explosives containing nitroglycerin imported during the year shows a slight falling off compared with 1903, the figures being 2,244,723 lbs. and 2,330,582 lbs. respectively; while the corresponding figures for blasting explosives not containing nitroglycerin are 252,606 lbs., and 168 lbs. and 2 cases respectively; a large proportion of the blasting explosives imported into England was for transshipment to other countries, viz., 1,759,652 lbs. out of 2,497,329 lbs.

During the year experiments were carried out at the Home Office Testing Station with the object of obtaining comparison between detonators charged with different compositions; details of these experiments are given in Appendix O (1). Other experiments were made to ascertain the liability to ignition by electric spark of dry nitro-cotton in a fine state of division. Only negative results were obtained.

A detailed account is also given of a series of experiments carried out in Belgium to determine the distances at which the explosion of varying quantities of dynamite would be felt in the open air; the results are given on pp. 63 and 64.

On October 24th, a new Order in Council was made, altering and extending the quantity of carbide of calcium which might be kept without a license. Originally the amount was restricted to 5 lbs., but it has now been increased to 28 lbs., provided notice is given to the local authority and certain precautions are observed.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 1, July 3, 1905.

Camphoacetic and β -Camphopropionic Acids.—A. Haller.—The author's researches show that though cyanosodo-camphor—except for certain exceptions which have been noticed—always behaves as an enolic molecule, methyl camphocarbonate can be considered as a β -ketonic body which gives carbon products when its sodium derivative is treated either with alcoholic iodides or sodium ethers. Owing to this property of camphocarbonic ether, its superior homologues can easily be prepared, using as an intermediary the double ethers to which the carboxymethyl group can be raised.

Synthesis of the Three Tertiary Dimethylcyclohexanols and the corresponding Hydrocarbides.—P. Sabatier and A. Mailhe.—Using the three cresols, the authors prepare ortho-, meta-, and paradimethylcyclohexane, and they find that the carbides thus obtained have very similar properties to those of the three dimethylcyclo-

hexanes which MM. Sabatier and Senderens prepared some years ago by the direct hydrogenation of the three xylenes. As for these latter carbides, the boiling-point of the ortho-derivative is much higher than that of the meta- and para-derivatives. The contrary is true of the corresponding alcohols, and also of the phenolic bisubstituted derivatives.

Preparation of Binary Compounds of Metals by means of Aluminium.—A. Colani.—Aluminium powder may be employed for the preparation of binary compounds in the absence of the electric furnace. Unfortunately, however, the products obtained generally contain a little aluminium and often iron also.

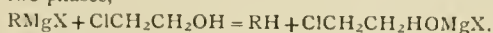
Constitution and Properties of Aluminium Steels.—Leon Guillet.—The author proves that aluminium has no important action on the mechanical properties of steel when it is present in quantity less than 2 per cent. Up to 15 per cent the aluminium enters into solution with the iron. The iron-aluminium solution thus formed does not dissolve carbon. It also takes a granular form, which explains the fragility of certain steels. Finally, in steels containing a large proportion of aluminium free martensite is found.

Compounds of Hydroferrocyanic and Sulphuric Acids. Sulphono-substitution in the Molecule of Complex cyanides. The Oxyferrocyanides.—Paul Chrétien.—The author prepares various compounds of hydroferrocyanic and sulphuric acids, and finds these substances decompose very easily in damp air, hydroferrocyanic acid being reproduced. The action of alkalis on the compound FeCy_6SO_2 is very remarkable, as it shows the absence of hydrogen in the molecule.

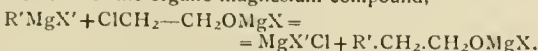
γ -Acid Aldehydes.—E. E. Blaise and A. Courtot.—The authors describe the preparation of the γ - $\alpha\beta$ -trimethyl and $\alpha\alpha$ -dimethyl- β -phenyl acid aldehydes. These two bodies are solid, and melt, the first at 63° and the second at 131° .

Synthesis of the Lactone of Erythric Acid.—M. Lespieau.—The lactone of erythric acid ($\text{C}_4\text{H}_6\text{O}_4$), which the author succeeds in synthesising, melts at 91° . It is very soluble in water and insoluble in ether.

New Method of Synthesis of Mono- and Polyatomic Alcohols.—V. Grignard.—The author's method consists in acting with the mixed organo-magnesium compounds of formula RMgX on the halogen derivatives of mono- or poly-atomic alcohols. Considering the preparation of glycol monochlorohydrine the reaction takes place in two phases,—



The complex thus obtained is capable of reacting on a new molecule of the organo-magnesium compound,—



β -Decahydronaphthyl Ketone and β -Decahydronaphthylamine.—Henri Leroux.—The author describes the preparation of various compounds prepared from the alcohol β -decahydronaphthol, which substance he investigated in a previous research.

New Derivatives of Mesoxalic Ethers.—Ch. Schmitt.—The author prepares the bisanilide of methyl mesoxalate, $(\text{CH}_3\text{CO}_2)_2\text{C}(\text{NHC}_6\text{H}_5)_2$, the bisanilide of ethyl mesoxalate, $(\text{C}_2\text{H}_5\text{CO}_2)_2\text{C}(\text{NHC}_6\text{H}_5)_2$, and the orthotoluide of methyl mesoxalate, $(\text{CH}_3\text{CO})_2\text{C}(\text{NH}_2\text{C}_6\text{H}_4\text{CH}_3)_2$, and investigates their properties.

Sparteine and its Action on Ethyl Iodide.—Charles Moureu and Amand Valeur.—During the action of ethyl iodide on sparteine, sparteine iodohydrate is formed, and two isomeric iodoethylates, either in a free state or combined with hydriodic acid.

Densities of Carbonic Anhydride, Ammonia Gas, and Nitrogen Peroxide.—Philippe A. Guye and Alexandre Pintza.—The authors find the mean values of the densities of the three gases, CO_2 , NH_3 , and N_2O , to be 1.9768, 0.7708, and 1.9774 respectively.

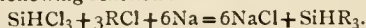
Thermo-chemistry of Neodymium.—Camille Matignon.—The author's investigations on the thermo-chemistry of neodymium show that this metal, and consequently the allied metals of the rare earth group, must be placed, from the point of view of their chemical affinity for the other elements, between the alkaline-earth metals and magnesium.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxviii., No. 7, 1905.

Methylazide.—Otto Dimroth and Wilhelm Wislicenus.—To prepare methylazide, sodium nitride (prepared by the action of ammonia gas upon sodium at 290–350° in a covered nickel vessel, or by the action of nitrous oxide upon sodium amide at 190°) is dissolved in water, the ammonia still present in the strongly alkaline liquid is completely expelled by a current of steam, and the solution is gently heated upon a water-bath in a flask fitted with a reflux condenser and a dropping funnel; dimethyl sulphate is then introduced, drop by drop, when methylazide is formed. It is purified and dried by passing through a U-tube filled with granulated calcium chloride and soda-lime, and heated to 25° to 30°, and is collected in a second U-tube, which is surrounded by a cooling mixture. Methylazide is a colourless liquid with a somewhat ethereal unpleasant odour, recalling that of hydrazoic acid. The combustion of the compound (performed with special precautions owing to its explosiveness) shows that the empirical formula is CH_3N_3 . The boiling-point is 20–21°, and the explosion temperature lies considerably above 500°.

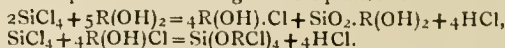
Quantitative Determination of Halogens in Chlorates, Bromates, and Iodates.—P. Jannasch and A. Jahn.—Red fuming nitric acid readily reduces potassium bromate and potassium chlorate quantitatively to bromide and chloride respectively. In the former case the flask in which the reaction takes place must be connected with a long Liebig's condenser to prevent the escape of bromine. Potassium iodate is not reduced quantitatively at ordinary pressures, but under increased pressure continued heating of it with silver nitrate and red fuming nitric acid causes the formation of the theoretical amount of silver iodide. Ordinary concentrated nitric acid when heated under pressure with chlorate and bromate will reduce them quantitatively, but not the iodate. This action of nitric acid is to be explained by the liberation of the halogen acid, which is then decomposed very readily in the case of chloric acid, and with great difficulty in the case of iodic acid. Hydrogen peroxide has no action in alkaline solution; in presence of nitric acid it reduces both chlorates and bromates, but not iodates. Hydrazine sulphate reduces potassium iodate and bromate very readily in alkaline solution, while the chlorate is scarcely attacked; formic acid behaves similarly, but with the iodate reduction proceeds until metallic iodine is separated. Grape-sugar and acetic acid under pressure yield the theoretical amount of silver chloride from chlorates. Reduction with hydroxylamine sulphate gave the best results; in acid solution the action is much stronger than in alkaline, metallic iodine being separated from iodates. Thus with chlorates, when the action is feeble, the reduction is best performed in acid solution, while with iodates and bromates the preference is to be given to ammoniacal solution.

Organic Silicon Compounds.—Fritz Taurke.—From silicon chloroform and N-propyl, isobutyl, and isoamyl alcohol in absence of moisture, the corresponding esters, $\text{SiH}(\text{OR})_3$, are formed, hydrochloric acid escaping. With aliphatic chlorides, silico chloroform and metallic sodium give the following reaction:—



This behaviour is noteworthy in view of the fact that with aromatic chlorides or bromides the tetra alkyl compounds are formed. With glycols silicon chloride first yields a glycol chlorhydrine, which then reacts like a monatomic

alcohol with more silicon chloride, giving the simple chlorinated alkyl ester of silicic acid of the formula $\text{Si}(\text{ORCl})_4$. It is best to employ, in the first instance, only as much silicon chloride as will yield the chlorhydrine, which is purified by distillation under normal pressure. More silicon chloride is then added to it slowly, and the reaction proceeds according to the equations:—



Simultaneously, white masses separate out; these were at first taken to be silicic acid, but on further examination were found to have a constant composition of 2 molecules of SiO_2 to 1 molecule of glycol. They may be a crystal alcohol, $2\text{SiO}_2\cdot\text{C}_2\text{H}_4(\text{OH})_2$, or else an acid ester of meta-silicic acid of formula $\text{SiO}(\text{OH})\cdot\text{O}\cdot\text{C}_2\text{H}_4\cdot\text{O}\cdot\text{SiO}\cdot\text{OH}$.

Action of Inorganic Compounds upon Optically Active Polyvalent Alcohols and Oxyacids.—Hermann Grossmann.—The salts of lead and bismuth are able, in presence of alkali hydroxides by substitution of atoms of hydroxyl hydrogen, to enter into the molecule of the higher alcohols and oxyacids, thereby causing extraordinarily great alterations in the specific rotation. The magnitude of the alteration varies very much in the mono-, di-, and tri-saccharides, which may perhaps throw some light upon the constitution of the polysaccharides. Alkaline lead solution, unlike uranium, tungsten, molybdenum, and boron compounds, reverses the direction of the rotation compared with that of the aqueous solution of the optically active compound. It was found that the action of lead acetate upon glucose in presence of sodium hydroxide caused a considerable increase in the specific rotation; in the case of fructose the rotation was turned from left to right. The occurrence of a maximum of rotation to the right when the molecular proportions were $2\text{C}_6\text{H}_{12}\text{O}_6 : 3\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, and the subsequent formation of complexes richer in lead, show that different lead fructosates exist in the solution; these the author is endeavouring to isolate. Bismuth nitrate increases the rotation of mannite. A specimen of ammonium titanium tartrate showed the following peculiar behaviour:—In concentrated solution the rotation is towards the left; it decreases with increasing dilution till finally it becomes a dextrorotation, and this continually increases as the dilution increases. Such behaviour has never before been observed with salts of d-tartaric acid, and proves the great complexity of the compound.

Reduction of Tetrathionate to Sulphite by Arsenite and Stannite.—A. Gutmann.—On evaporating solutions of sodium arsenite and tetrathionate over sulphuric acid, sulphite, monosulphoxyarsenate, and tertiary sodium arsenate are obtained. No sodium sulpharsenate nor disulphoxyarsenate is formed. One molecule of tetrathionate always gives rise to 1 molecule of arsenate, decomposing according to the equation $\text{S}_4\text{O}_6 = \text{O} + \text{S}_2 + 2\text{SO}_2$. Sodium stannite reduces tetrathionate in alkaline solution to sulphite, sulphostannate and stannate being formed at the same time; under some experimental conditions some stannous sulphide is obtained.

Ketenes.—Hermann Staudinger.—The author has succeeded in isolating a substance of the formula $(\text{C}_6\text{H}_5)_2\text{C}:\text{CO}$, belonging to the hitherto unknown type $\text{R}_2\text{C}:\text{CO}$, to which he has given the name ketene. Diphenyl ketene is prepared by gently heating diphenyl-chloroacetyl chloride with zinc turnings and ether; the zinc chloride formed is precipitated with petroleum ether, and on distilling off the solvents the ketene remains behind as a brown oil. Diphenyl ketene is very reactive, and is oxidised when exposed to the air. In many respects its behaviour resembles that of the analogous isocyanic acid ester, $\text{RN}:\text{CO}$. With water the ethereal solution gives diphenyl acetic acid. With perfectly dry chlorine it yields diphenyl acetyl chloride, but if any moisture is present in the chlorine diphenyl acetic acid ethyl ester is formed. In cold benzene solution it is far more stable towards water than in ethereal solution.

MISCELLANEOUS.

The Paper Makers' Directory of all Nations.—We have just received this useful Directory for the year 1905; it is published by Messrs. Dean and Son, Limited, and contains all the principal paper, pulp, and board mills of the world. The work is alphabetically arranged throughout according to countries; the mills—some 5000 in all—being again set out under each country in a similar manner, and at the end of every section a classified list of the mill productions is given. Many useful hints are included, and the names of cardboard and paper box manufacturers, as well as those of china-clay dealers, have been added, so that this, the fourteenth, edition has been further increased by the addition of 20 pages.

Merck's Annual Reports, Vol. xviii., 1904.—These Reports are now so well known that little comment on their excellence is needed. They are widely appreciated and consulted as books of reference on pharmacology and therapeutics. Not only are Messrs. Merck's own new products specially mentioned, but the same treatment is unstintingly extended to interesting and valuable preparations originating from other sources. The present volume consists of 250 pages, and is sent free to medical men and others interested, on application to the London office at 16, Jewry Street, E.C.

Institute of Chemistry of Great Britain and Ireland.—Pass List of the July Examinations.—Of 19 Candidates who entered for the Intermediate Examination, 12 passed:—J. W. Agnew, H. G. Dale, James Dick, junr., W. P. Hayworth, I. M. Heilbron, R. F. Innes, S. Judd Lewis, A. J. C. Lickorish, F. L. Okell, R. P. Page, H. J. B. Rawlins, B.Sc. (Lond.), and D. R. Wood. In the Final Examination for the Associateship (A.I.C.), of 5 examined in the branch of Mineral Chemistry, 3 passed:—J. B. Hoblyn, Assoc.R.C.Sc. (Lond.), G. W. James, B.A. (Oxon.), and H. H. Kingdon, B.A. (Oxon.); of 6 in Organic Chemistry, 4 passed:—A. W. Bain, B.A., B.Sc. (Lond.), T. W. Cheke, J. Stuart Hills, and D. F. Twiss, M.Sc. (Birm.); and of 9 who entered in the branch of the Analysis of Food and Drugs and of Water, including an Examination in Therapeutics, Pharmacology, and Microscopy, the following 4 passed:—R. W. Blair, Assoc.R.C.Sc.I., P. H. Carpenter, J. A. Goodson, and S. Summerson, B.Sc. (Lond.). One Candidate passed an Examination for the Fellowship (F.I.C.):—E. F. Harrison, B.Sc. (Lond.). The Examiners in Chemistry were Mr. W. W. Fisher, M.A., F.I.C., of Oxford, and Dr. G. G. Henderson, M.A., F.I.C., of Glasgow. The Examination in Therapeutics, Pharmacology, and Microscopy was conducted by Dr. F. Gowland Hopkins, M.A., M.B., F.R.S., F.I.C., of Cambridge.

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MICHAELMAS TERM.—Monday, October 2, to Saturday, December 16.

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EASTER TERM.—Monday, April 30, to Saturday, July 21.

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Arrangements have been made with leading Engineering Firms in Edinburgh and elsewhere, whereby Students may combine their Apprenticeship with their studies at the College. A similar arrangement has been made for Brewers' Apprentices, and special facilities are offered to Chemistry Students for the study of the Analysis of Fuels, Gases, and Coal Distillation By-products in the Laboratories of the Corporation's Gas Works.

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PETER MACNAUGHTON, S.S.C., Clerk.

20, York Place, Edinburgh,
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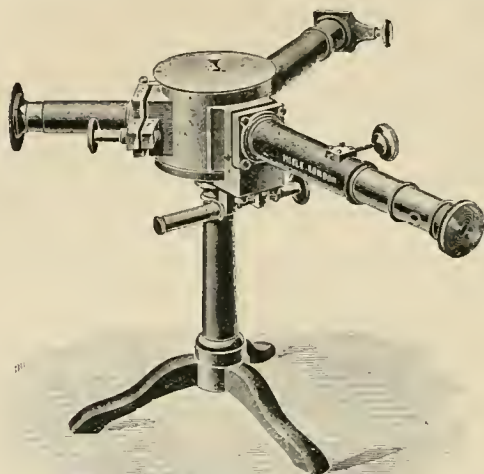
The Session 1905-6 commences October 2nd, 1905.

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THE CHEMICAL NEWS.

VOL. XCH., No. 2385.

WEATHERED HAY.

By W. F. SUTHERST, Ph.D., F.I.C.

DURING our haymaking period we were interrupted once by wet weather, which gave me the opportunity of finding out what effect the rain had on the constituents of the hay, with regard to their removal. A portion of the hay in the field, consisting principally of rye-grass, was protected from the rain, which lasted interruptedly for two days, and was then exposed to the sun with the rest. When dried it was analysed for the following constituents:—Moisture, albumenoids, carbohydrates, fibre, and ash.

The albumenoids were found by the Kjeldahl method, using a drop of mercury to hasten the reaction; the resulting nitrogen found being multiplied by 6.5. Fibre and carbohydrates, the latter by difference, by boiling a sample first with 5 per cent H_2SO_4 , then with 5 per cent KOH , removing the carbohydrates and albumenoids respectively. The following results were obtained:—

	Water.	Albu- menoids.	Carbo- hydrates.	Ash.	Fibre.
Ordinary hay	15.65	16.52	39.14	5.43	28.91
Weathered „	12.75	14.58	37.14	4.96	33.32

All the constituents are calculated on dry matter.

It will be seen from the above results that first of all there is less water in the weathered hay; this seems at first curious, but it may be explained that the gummy substance in hay, which would be the first to be washed out, is hygroscopic, and attracts atmospheric moisture, whilst in the weathered portion this property would be present in a less degree.

The loss of two parts (14 per cent of total) of the nitrogenous substances is not so serious as might be expected, since the soluble nitrogenous bodies would be the amido-compounds, whose food value is very small; the more valuable albumenoids, being less soluble, remaining behind. The ash is of course less, since every part of hay contains ash, and the fibre being quite insoluble in water is undisturbed.

The Agricultural College, Tamworth.

THE ESTIMATION OF THE SILICA IN SUB-CARBONIFEROUS LIMESTONE.

By NICHOLAS KNIGHT.

THE specimen of the subcarboniferous limestone used in this work was obtained from a quarry near Bedford, Indiana, and it is known locally as the Bedford limestone. It is a light coloured rock, fine grained in texture, and it is widely used and favourably regarded as a building material.

The amount of residue insoluble in hydrochloric acid, which proved to be mainly silica, was determined by three different methods as follows:—

Method 1.—A gm. of the fine powder was placed in a small beaker covered with a watch-glass. Dilute hydrochloric acid was added, and the contents of the beaker gently heated to boiling. After standing a short time, the undissolved portion was filtered off, and the weight determined.

Method 2.—A gm. of the powder was placed in a porcelain evaporating dish, and while covered with a watch-glass, dilute hydrochloric acid was added. It was

left on the water-bath until effervescence ceased, the accumulations on the watch-glass were rinsed off, and the evaporation continued until crystals began to appear. Then as the evaporation went forward, the substance was stirred with a glass rod until a fine dry powder resulted. This was moistened with concentrated hydrochloric acid, and left on the water-bath for a few moments. Dilute hydrochloric acid and water were added, and after standing a short time the insoluble residue was filtered off, dried in the air-bath, and its weight determined. The insoluble residue was obtained three different times by each of the two methods, varying the weight of the original amount taken. The results were as follows:—

	Method 1.	Method 2.
(a) With 1 gm. substance..	0.54 per cent	0.65 per cent
(b) „ 3 grms. „ ..	0.56 „	0.55 „
(c) „ 10 „ „ ..	0.55 „	0.55 „

To determine further the nature of the residue, whether it was all silica, or wholly or partly a silicate, it was treated in the platinum crucible with a few drops of dilute sulphuric acid, and the crucible was nearly filled with a dilute solution of hydrofluoric acid. It was evaporated on the water-bath, and the excess of sulphuric acid removed with the free flame.

Residue in the Crucible obtained by Methods 1 and 2.

	Method 1.	Method 2.
(a) 1 gm. substance..	0.13 per cent	0.13 per cent
(b) 3 grms. „ ..	0.12 „	0.12 „
(c) 10 „ „ ..	0.14 „	0.11 „

A blank test was made, using sulphuric and hydrofluoric acid in the crucible, and evaporated to dryness. No residue was obtained.

The residue in the crucible was determined and found to be:—

Aluminium and iron sulphate ..	0.08 per cent
Calcium sulphate.. ..	0.058 „
Magnesium sulphate	0.00 „
	0.138 „

Method 3.—To compare the insoluble residue obtained by fusion with alkaline carbonate with the amount obtained by the foregoing methods:—

A gm. of the fine rock powder was thoroughly mixed in the platinum crucible with 7 grms. of anhydrous sodium carbonate. The sodium carbonate used was a good quality of Merck's manufacture. It was further purified by dissolving a quantity in water and filtering. This after fractional crystallisation seemed to be entirely free from silica. The covered crucible was heated for fifteen minutes with a Bunsen flame, then with a blast-lamp to complete fusion. The cooled mass was transferred to a porcelain evaporating dish, and dissolved in dilute hydrochloric acid. Evaporation was continued on the water-bath until crystals began to appear. It was then stirred with a glass rod until a fine dry powder was obtained. It was treated with hydrochloric acid as in Method 2 before described. The insoluble residue obtained by this method amounted to 0.53 per cent. This treated with sulphuric and hydrofluoric acids left a residue of 0.16 per cent. The results are fairly concordant with those obtained by Methods 1 and 2, but on account of the difficulty of getting pure sodium carbonate and the length of time and the labour necessary to obtain the result, this process is not to be commended in rocks of this character. Indeed, Method 1 is greatly to be preferred whenever circumstances permit, on account of its simplicity and the shortness of the time required.

During the course of this work our attention was called to the estimation of silica as outlined by Treadwell in his excellent treatise on quantitative analysis (Treadwell-Hall, "Quantitative Analysis," p. 384). After removing the insoluble residue according to Method 2, it is stated that "as much as 5 per cent of the total amount (of silica) may

remain in the filtrate. In order to remove this, the filtrate from the first precipitate is once more evaporated to dryness on the water-bath, and kept on the water-bath for one or two hours or more.* It is then filtered after treatment with hydrochloric acid and water in the usual manner. One grm., 5 grms., and 10 grms. of substance were used. In no case was even a trace of residue obtained by the second treatment. The experiment was varied by using a specimen of argillaceous limestone that contained 18 per cent of silica.

A second portion of residue could not be obtained from this specimen.

A complete analysis of the Bedford limestone resulted as follows:—

CaCO ₃	93.55 per cent
MgCO ₃	5.42 "
SiO ₂	0.55 "
Fe ₂ O ₃ and Al ₂ O ₃	0.50 "
	100.02 "

The condition of the iron was tested by placing 3 grms. of the powdered rock in a flask of 120 c.c. capacity, fitted with a bulb-tube and Bunsen valve. The material was dissolved in a small quantity of dilute hydrochloric acid. A few drops of the solution quickly withdrawn and placed on a porcelain tile in contact with a solution of potassium ferricyanide showed a slight tinge of blue. A few drops of a solution of potassium sulphocyanate were then quickly introduced into the flask, when a red colour was produced. The portion of the iron soluble in hydrochloric acid is therefore of both the ferrous and ferric forms. No attempt was made to determine each quantitatively on account of the small amount.

The writer acknowledges the assistance of Alys Boies Carson for making the experiments in this investigation.

Chemical Laboratory, Cornell College.
July 4, 1905.

ON THE OXIDATION OF PHOSPHORUS.

By W. P. JORISSEN.

1. In the discussion following the reading of the paper on "The Mechanics of Fire," by Prof. Armstrong, in the London Section of the Society of Chemical Industry (*Journ. Soc. Chem. Ind.*, May 15th, 1905), Dr. Brereton Baker made the following interesting statement:—

"He took three similar bits of glowing phosphorus, placed them in lead tubes, and over them a photographic plate in the dark. He wanted to measure the amount of light given out by these pieces of glowing phosphorus. One tube was charged positively from a large accumulator, another was charged negatively, and the third was left uncharged. The phosphorus was just moist enough to become a conductor. He left it about half-an-hour, and then developed the plates; under the positive tube he found a black mark; under the negative scarcely any; and the third was about the mean of the other two. That was only one experiment, and many more would be required to confirm the observations. It seemed to him this experiment, which of course required confirmation, might throw some light on the question as to whether ions were really produced, the positive ions of oxygen being attracted to one side, and the negative ions to the other. There were very few positive ions combining with the phosphorus; what became of them? They all knew that when phosphorus glowed ozone was produced. He did not measure the ozone coming from each piece of phosphorus, but if the hypotheses formed were correct, he would find little ozone at the positive phosphorus, whilst much would be produced at the negative."

This leads me to communicate that last year the following experiments were made by me (*Chem. Weekblad.*, 1904, i., 341):—Three photographic plates were wrapped in black paper in such a manner as to be wholly protected from the influence of the light. On each of them a very thin piece of mica was placed, and on this a small lump of phosphorus. They were covered by glass beakers, under two of which were put a very small dish with some ether and one with some turpentine-oil respectively.

In the dark it appeared that the phosphorus only glowed under the beaker, which did not contain any vapour of ether or turpentine-oil, as was to be expected.

After some seven hours it was only the plate exposed in this way to the action of the oxidising phosphorus that on developing was found to have been acted upon. An image of the mica film was seen on the darkened plate; but also an action had taken place under this film. The darkening ceased at the brim of the beaker.

These experiments were repeated after placing thin films of gold and silver over the plates. The result was the same; only on the place where two films had been put on top of each other, the darkening was somewhat less.

That Knoblauch had made an observation of the same kind was unknown to me at the time of my experiments. Some months ago I found in a paper of Bredig and Pemsel (*Arch. f. Wissensch. Photogr.*, 1899, i., 33), just then sent to me by the authors, the following communication:—"M. Knoblauch kindly informs us that phosphorus, like uranium, issues a photographic radium-like action which also penetrates through untransparent substances." It would be interesting to test also other spontaneously oxidising substances in this way. Frantz (*Zeit. f. Elektrochem.*, 1904, x., 593), who studied the luminous glow seen during several oxidation processes (Radziszewski, *Liebigs Ann.*, 1880, cciii., 305–336; Perkin, *Journ. Chem. Soc. Trans.*, 1882, xli., 363) and crystallisations, remarks:—"In more than one case, when during crystallisations and reactions a glow was observed, the rays were found to penetrate through black paper. Still a very prolonged exposure is necessary."

2. To these experiments I was led by the well-known observations about the ionisation of oxygen of the air in contact with phosphorus. In the first place, I mention the fact that the air, in which oxidation of phosphorus takes place, becomes a far better conductor for electricity than ordinary air, and that particles with opposite charges are to be found in the neighbourhood of oxidising phosphorus.* Traces of turpentine-oil, ether, and carbon disulphide, which among many other substances have the power of preventing (or delaying) the oxidation of phosphorus at a certain pressure of the oxygen (Joubert, Thèses, Paris, 1874, 43–45; Centnerszwer, *Zeit. f. Phys. Chem.*, 1898, xxvi., 3), remove this conductivity (Elster and Geitel, *Edgar Meyer and E. Müller, loc. cit.*).

In the second place, I mention the condensation of a steam jet in the presence of slowly oxidising phosphorus observed by R. von Helmholtz and Richarz.† Also when the luminous vapour is blown aside the action on the steam jet is not diminished. It is, however, not affected by ozone, hydrogen peroxide, or nitrous acid.

In the third place, I wish to draw attention to a very interesting observation made by van't Hoff (*Zeit. f. Phys.*

* See the papers mentioned by J. J. Thomson in his "Conduction of Electricity through Gases," 1903, 324; also Elster and Geitel, *Wied. Ann.* 1890, xxxix., 322; *Phys. Zeit.* 1903, iv., 457; Harms, *Handbuch der Radioaktivität und Elektrizität*, 1904, i., 293; Edgar Meyer and E. Müller, *Ber. Deutsch. Phys. Gesell.*, 1904, ii., 332; Bloch, Thèses, Paris, 1904, "Le Radium," August 15th, 1904.

† R. von Helmholtz and Richarz, *Wied. Ann.*, 1890, xl., 192; see also J. J. Thomson, *loc. cit.*, p. 134. Helmholtz and Richarz also observed an action of nitrogen oxide, ether, potassium, and sodium. In connection with my experiments on the activation of oxygen (*Zeit. f. Phys. Chem.*, 1897, xxii., 34; 1897, xxiii., 667; *Arch. Neel.*, 1897; see also J. W. Mellor, "Chemical Statics and Dynamics," 1904, 306), I also tried and found to act on the steam jet triethylphosphine, benzaldehyde, turpentine-oil, and a strong solution of sodium sulphite, all in the act of oxidation, their surfaces being enlarged by bringing some drops of them on a piece of blotting-paper (*Chem. Weekblad.*, 1904, i., 341).

Chem., 1895, xvi., 411). He shook a small quantity of phosphorus with a solution of indigo sulphonic acid and air, after having heated the vessel with the solution in water of 50° C. After violently shaking about thirty times, he put it in the water again. A kind of flame appeared and died away, only to reappear after repeated shaking.

About 9 m.grms. of phosphorus had not quite disappeared after the flame had returned 277 times. "According to the above mentioned flame phenomenon," he says, "something is present in the atmosphere of the vessel which prevents the phosphorus from oxidising; there is apparently enough oxygen left; there might be supposed to be a lack of phosphorus-vapour. On opening the vessel, however, the opposite is proved by the now appearing phosphorescence. On shaking with indigo, the hampering action, which I am inclined to ascribe to the electric charge, respectively to the positive or negative oxygen ions in excess, is annihilated, while sulphuric acid (perhaps on account of its conductivity) accelerates it in a high degree. And that the act of shaking, which enables the oxidation to take place again, is not to be attributed to saturating with phosphorus-vapour, is shown by the fact that without indigo, with phosphorus and water only, the whole of the typical flame phenomenon is not produced."

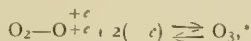
Speaking about the above named oxygen ions he says:—"If the pieces in question are charged positively and negatively, it may be easily understood that the substance, which is oxidised, prefers one of them, while the other gives an electric charge to the oxygen, which ends in the formation of ozone, the decolouration of indigo, &c."; and further, "the primary product formed in oxygen, which has been made active by phosphorus, is not ozone, for it prevents the phosphorescence of the phosphorus, while ozone favours this phenomenon" (*Chappuis, Bull. Soc. Chim. de Paris*, 1881, xxxv., 419).

3. R. von Helmholtz and Richarz concluded from their experiments, referred to above, that the action on the steam jet is caused by pairs of atoms, —O—O—, or by free atoms of oxygen.

The conclusion to which van't Hoff came has been already quoted.

Thirdly, as regards the ionisation of the oxygen during the oxidation of phosphorus and the kind of ions formed, I wish to refer to J. J. Thomson's "Conduction of Electricity through Gases," 1903, 324—325, to J. W. Mellor's "Chemical Statics and Dynamics," 1904, 309—312, and to the following papers:—E. Bloch, *Thèses*, Paris, 1904, "Le Radium," August 15th, 1904; F. Harms, *Fahrbuch der Radioaktivität und Elektronik*, 1904, i., 291).

Somewhat more extensively I wish here to treat of the reasoning of R. Schenck (*Sitz. Berichte Akad. Wissensch. Berlin*, January 7th, 1904). He remarks that without doubt during the oxidation of phosphorus electrons are formed, and that these transform oxygen into ozone. This formation of ozone, however, is not complete. He supposes an equilibrium to arise between oxygen, ozone, oxygen atom ions, and electrons, which may be represented by the symbol—



in which by O^{+e} an oxygen atom ion and by $-e$ an electron is meant.

He now supposes that the phosphorus or one of its products of oxidation (see Jungfleisch, *Comptes Rendus*, 1905, cxi., 444) becomes luminous under the influence of the ionised oxygen, and that the oxidation of the phosphorus takes place by means of oxygen atom ions.

"If now," he says, "we increase the pressure of the oxygen, the concentration of the ozone will become greater at the expense of the ions. If the concentration of the oxygen increases sufficiently, the number of the ions will at last grow smaller than the quantity which is required to

make the light perceptible to the eye. Hand in hand with this phenomenon goes the decrease of the reaction velocity according to the law of mass action."

Against this conclusion of Schenck the following may be argued:—

From the equilibrium supposed by him follows:—

$$\frac{\text{C}_{\text{O}_2} \cdot \text{C}_{\text{O}^{+e}} \cdot \text{C}_{-e}^2}{\text{C}_{\text{O}_3}} = k \dots \dots (1).$$

Now the concentration of the oxygen is very considerable in comparison with the other concentrations; thus we may write with some approximation:—

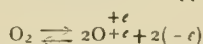
$$\frac{\text{C}_{\text{O}^{+e}} \cdot \text{C}_{-e}^2}{\text{C}_{\text{O}_3}} = k' \dots \dots (2).$$

Now, if the degree of ionisation decreases, the concentration of the ozone must become smaller and not greater as Schenck concludes.

The fact that phosphorus which does not glow, because the pressure of the oxygen is too high, becomes luminous if a trace of ozone is added, corresponds with formula (2) if we suppose that Schenck's hypothesis about the glowing of phosphorus by means of oxygen ions is a fact.

For, if the concentration of the ozone—which may be put as zero in oxygen in which phosphorus does not glow—is increased, the concentration of the ions will do the same. Now, according to Schenck's reasoning, the concentration of the ozone in the neighbourhood of the "boundary-pressure" of the oxygen would be considerable, which is not according to facts.

If, however, with van't Hoff we suppose the equilibrium



to exist,* then the degree of ionisation will become smaller on our increasing the pressure of the oxygen, without having to assume an increase of the ozone-concentration. The ionised oxygen will indeed have a larger volume than the ordinary oxygen.

But our views will remain incomplete if we cannot bring into account the influence of water vapour on the boundary-pressure of the oxygen. In this respect also a closer study of this pressure is important.

Helder, Holland, June, 1905.

City and Guilds of London Institute.—At a meeting of the Council held July 24th the diploma of "Associate of the City and Guilds Institute" was awarded to the following matriculated third-year students of the Central Technical College who have completed a full course of instruction as prescribed by the Council:—*Civil and Mechanical Engineering*.—C. J. Balding (Bramwell Medal), R. W. Allen, C. M. Baissac, A. M. Beale, G. E. W. Bridge, R. W. Buttemer, F. C. Cooper, J. A. Denney, L. J. M. Guggenheim, G. W. Halse, C. Herbert, J. Hodgkinson, C. B. Job, I. King, S. Lacy, A. J. H. Laing, A. R. Mitchell, J. E. Montgomery, K. Newton, A. R. Reed, L. M. Regnard, G. M. Smith. *Electrical Engineering*.—W. H. Grinstead (Siemens Medal and Premium), A. J. Aldridge, C. R. Bland, E. B. Brown, J. L. Cook, P. G. Dani, P. Eisler, R. R. Elliott, O. Faber, W. M. Hooton, H. R. Hudson, G. Johnson, N. H. Martin, C. R. McGowan, C. E. Nightingale, H. K. B. Reed, F. C. Street, F. W. Strickland, K. J. Thomson, F. L. N. Tuck, W. Turner, A. Vipan, E. C. Webber. *Chemistry*.—W. H. Eagle, F. J. Harris, W. J. Wilson.

In 1895, when van't Hoff (*Zet. f. Phys. Chem.*, 1895, xvi., 411) supposed the equilibrium $\text{O}_2 \rightleftharpoons 2\text{O}$ to exist in oxygen, also if a spontaneously oxidising substance is absent, the hypothesis of the electrons had not been brought forward as it is now.

* Schenck uses another symbol which comes to the same thing; the above seems to me to be more evident.

THE HANDLING OF PRECIPITATES FOR
SOLUTION AND RE-PRECIPITATION.

By F. A. GOOCH.

In many processes of analytical chemistry, the preparation of substances in pure condition is brought about by precipitation, solution, and re-precipitation; and sometimes this cycle of operations must be repeated. When a precipitate, gathered upon a filter, is easily acted upon by the appropriate solvent, the process of dissolving the precipitate from the filter is simple; but when the precipitate is refractory toward solvents or difficult to attack on account of its physical condition, as is the case with many gelatinous precipitates, the proper handling of the precipitate involves some inconvenience and delay.

In meeting such difficulties, I have found it advantageous to place within the ordinary paper filter, before filtering, a movable lining of platinum gauze, upon which the precipitate rests for the most part and with which it may be removed. The simplest form of this device is easily made by cutting platinum gauze to the shape shown in Fig. 1.



FIG. 1.

In ordinary use, this piece of gauze, folded to make a cone of angle a little less than 60° , and held by pincers at the point of overlapping, is placed within this filter and allowed to fit itself closely by the natural spring of the gauze when released.

Upon filters so prepared a precipitate may be collected and washed as usual; and, at the end of the operation, the cone with nearly all the precipitate may be transferred, by means of ivory-pointed pincers, to dish or beaker for suitable treatment. The small amounts of the precipitate which have passed through the gauze, being somewhat protected by the gauze against the compacting action of filtration and washing, are generally removable with ease from the filter by a jet of the washing-liquid. After washing, the gauze may be replaced within the same filter and serve for a second collection of the precipitate to be subsequently dissolved, in case double precipitation and solution are desirable. The final collection of the precipitate is, of course, made upon paper without the gauze lining, when precipitate and filter are to be ignited.

This device has proved very serviceable in the handling of such precipitates as ferric hydroxide, aluminium hydroxide, and basic acetate precipitations.

I have used also in the manipulations of such precipitates a regularly made cone of 60° , fitted with eyelets for handling; but the simple folded cone is, on the whole, more convenient.

Precipitates collected upon asbestos in the perforated crucible are frequently removable without difficulty by allowing a suitable solvent to percolate precipitate and felt; but in case the precipitate is pasty or compacted, solution in this manner may be unpleasantly slow. In such cases, it is convenient to remove the greater part of the precipitate, collected and washed in the usual manner, upon a disc of platinum foil, perforated, fitted with a wire handle, as shown in Fig. 2, and placed upon the asbestos felt before the transfer of the precipitate to the crucible. To make such a disc is the work of a few moments only; and by its use pasty precipitates, such as cuprous sulphocyanide

or the sulphides of the metals, are easily handled for solution.



FIG. 2.

These simple devices so facilitate the manipulation of precipitates in many processes of analysis that they have seemed to be worthy of description.—*American Journal of Science*, xx., July, 1905.

THE ASSAYING OF TIN AND TERNE DROSSES.

By GEORGE P. MAURY.

THESE drosses are a heterogeneous mixture of the metal buttons from about 5 grms. in weight down to a size that will pass through about a forty mesh sieve, with oxides of tin, lead, iron, and zinc, zinc chloride, silica, alumina, partly burned carbonaceous matter, &c. It can readily be seen that a very large variation in results may occur unless special precautions are taken to put the sample in such shape that a correct average may be obtained in the portion taken for the assay.

The dross is received in two portions, together with the percentage of each in the car sample; the coarse, that did not pass through a twenty mesh sieve, and the fine, that did pass through a twenty mesh sieve in sampling.

The relative amounts of fine and coarse vary widely, running from 0.25 per cent coarse to 0.20 per cent coarse, depending upon the richness and physical condition of the dross.

The conditions naturally divide the method of analysis into, and we shall consider it under three heads:—"The Preparation of the Sample," "The Assay," and "The Analysis of the Button from the Assay."

Preparation of the Sample.

Under this head I will describe two methods, either of which gives good results:—

Method by oxidation.

Method of separating the coarse from the fine, and weighing each portion.

Method of separating the coarse from the fine.

For convenience we will call the original coarse sample A and the original fine sample B; for example, we take a dross containing 10 per cent coarse, which we call A, and 90 per cent fine, which we call B.

All of A is taken, in this case 200 grms., ground until everything will go through a one hundred mesh sieve, except the metal beads or buttons; these are flattened out—the object in so doing is to be sure that all the small pieces of brick, gravel, &c., are broken up, and to know that nothing of the kind is left with the buttons of metal; after this operation there are (see calculation) 50 grms. of fine, equal to 25 per cent, and 100 grms. of coarse, equal to 75 per cent.

For a 300 gm. sample, there would be 10 per cent of 300 grms., or 30 grms. of A, and 90 per cent B, which is equal to 270 grms.

The 270 grms. are ground until everything except the metallic buttons will pass a one hundred mesh sieve, the buttons are flattened as described above under the coarse. Upon weighing the coarse and the fine, the coarse from B equals 30 grms., which is 11.11 per cent, and the fine equals 240 grms. or 88.89 per cent. The coarse from A was 75 per cent, and there would be required for a 300 grm. sample 30 grms. of A; then 75 per cent of 30 grms. equals 22.50 grms. from A, and 11.11 per cent of B equals 30 grms. of coarse, or a total of 52.50 grms., equalling 17.50 per cent of coarse.

These amounts are weighed out and mixed.

For the fine we had 25 per cent of B or 25 per cent of 30 grms., equal to 7.50 grms. Of the fine in B there was 88.89 per cent of 270 grms., equal to 240 grms.; a total of 247.50 grms., equal to 82.50 per cent of 300 grms., the amount of the sample taken. These are thoroughly mixed.

Then the assay sample will consist of 17.50 per cent coarse and 82.50 fine. On a 20 grm. assay this would be 3.50 grms. of coarse and 16.50 grms. of fine.

Calculation.

10 per cent coarse A	300-grm. sample	{	30 grms. of A
90 per cent fine B..	equals	270	" " B
A yields	Fine.. 50 grms. equals	25	per cent
B yields	Coarse 150 " "	75	" "
	Fine.. 240 " "	88.89	" "
	Coarse 30 " "	11.11	" "

New sample :—

Coarse	10 per cent of A equals 30 grms.,	75	
	per cent of which is coarse equal to		22.50 grms.
	90 per cent of B equals 270 grms.,		
	11.11 per cent of which is coarse		
	equal to	30.00	"
	Total coarse equals 17.50 per cent	52.50	"
Fine	A 10 per cent of 300 equals 30 grms.,		
	25 per cent of which is fine equal to	7.50	"
	B 90 per cent of 300 equals 270		
	grms., 88.89 per cent of which is		
	fine equal to	240.00	"
	Total fine equals 82.50 per cent	247.50	"

Assay | Coarse = 17.50 % for 20 grm. - { 3.50 grms. coarse
sample | Fine = 82.50 % sample .. { 16.50 " fine

Oxidation Method.—About 400 grms. of the sample accurately weighed are taken, placed in a large evaporating dish (12 in. in diameter) moistened with water, and nitric acid added very cautiously at first, then heat gently until solution is complete. It usually takes about as many c.c. of nitric acid to oxidise sample as grms. of sample taken (this may vary, of course, as the dross is rich or lean in metallic particles). Add cautiously enough sulphuric acid to replace nitric acid left (usually about one-third to one-fourth of amount of nitric used), evaporate to dryness, and heat to drive out nitrates and as much sulphuric acid as possible, break up mass, and grind to pass a 100 mesh sieve, then heat to a red heat for at least one hour to decompose all sulphates (to prevent trouble from boiling over the top of the crucible, also to reduce amount of potassium cyanide required in assay), allow sample to cool, and weigh accurately; sample will weigh more on account of oxygen taken up.

We find it weighs 504 grms., which divided by 400 (amount of the sample taken) equals 1.26, which is the factor by which to multiply the result obtained in assaying; that is, if the sample shows 30 per cent of the metal by assay, this multiplied by 1.26 equals 37.80 per cent the amount in the original dross.

The Assay.—Take 20 grms. of the sample and 100 grms. of potassium cyanide in a "G" or "J" crucible, mix the sample with about 50 grms. of the ground cyanide, and place about 40 grms. of the balance in the bottom of the

crucible, then add the sample mixed with the cyanide, settle well by tapping, and add the balance of the cyanide, spreading it in a thin layer over the top of the sample.

A blacksmith's forge is used to reduce the assay, and it is very satisfactory. While authorities on assaying tell you to use a bright red or white heat, our best results have been obtained above a white heat, in fact as high as an air blast and a coke fire will give in a forge just short of melting a Denver crucible.

High temperatures have given the highest results and low temperatures invariably give low results. The crucible is allowed to stay in the furnace from five to ten minutes after fusion begins. The high iron content in the dross and the button raises the fusion point of the button, and makes the high temperature necessary for a correct assay. The crucible is allowed to cool, and is broken, the button is thoroughly cleaned, boiled in water, dried, and broken up by hammering, and is washed again in boiling water, dried, and weighed as a check on the direct determinations of the contents of the button.

Analysis of the Button.—After weighing the button it is dissolved in hydrochloric acid with a small amount of nitric acid, diluted to 1 litre, and 50 c.c. or one-twentieth of the solution taken for the determination or iron by titration with potassium bichromate.

Fifty c.c. is taken for the determination of tin, copper, zinc, and lead; this is made nearly neutral, 30 c.c. of ammonium sulphide solution added, and digested for about thirty minutes. Hydrogen sulphide is passed through the solution, and the solution filtered. The iron, lead, copper, and zinc are dissolved off the paper with strong hydrochloric acid and a few drops of nitric acid, boiled, and brought nearly to neutral point with ammonia; 30 c.c. more ammonium sulphide added, and digested as before. Usually three ammonium sulphide separations are necessary to separate the tin from the other metals.

The iron, lead, &c., are then dissolved as before, sulphuric acid added, and evaporated until fumes of sulphuric anhydride are given off, for lead by the sulphate method. Make double hydrate of filtrate for zinc, and determine by hydrogen sulphide and sodium carbonate.

The precipitate of iron is next dissolved and tested with hydrogen sulphide to see if any tin has gone through with the iron.

The filtrates from the ammonium sulphide digestions are combined and made slightly acid with sulphuric acid to precipitate the tin as a sulphide; it is filtered, thoroughly washed with hot water, burned, and weighed.

Extreme care is exercised to prevent volatilisation of tin as proto-sulphide. Ammonium carbonate is added to remove the last of the sulphuric anhydride.

When percentage of iron is high in an alloy of tin and iron, the separation of tin by oxidation with nitric acid is unsatisfactory, as part of the iron will be carried down with the oxide of tin, and some of the tin will go in solution with the nitrate of iron.

Separation of tin and iron by hydrogen sulphide in acid solution gave very unsatisfactory results; if the solution is acid enough to hold up the iron, some of the tin will be held in solution, and if all the tin precipitates some iron will be carried down with it.

The separation with sodium sulphide proved unsatisfactory on account of trouble in washing out sodium salts.—*Proceedings of Engineers' Society of Western Pennsylvania*, xxi., No. 2.

Chromic Sulphate.—Albert Colson.—The solution of a metallic oxide in an acid diluted with water by definition gives a dissolved salt. This is neutral, acid, or basic, according to the proportion of the reacting substances, and should preserve the essential chemical properties of the species of salt obtained. The author now shows that the solution of chromic oxide in dilute cold sulphuric acid gives a variety of sulphate in which the sulphuric acid resists all reagents.—*Comptes Rendus*, cxli., No. 2.

ELECTROLYTIC OXIDATION OF
HYDROCARBONS OF THE BENZENE SERIES.*

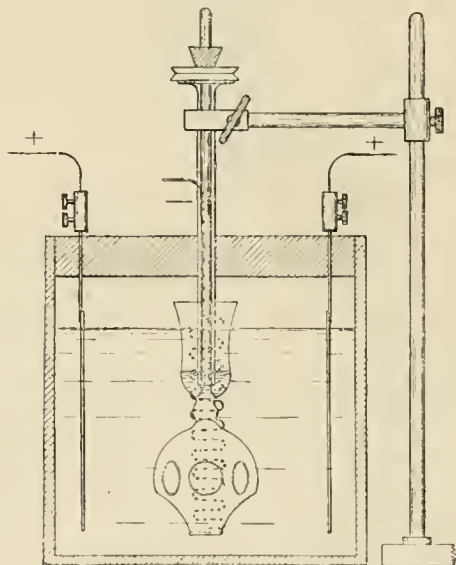
PART II. ETHYLBENZENE, CUMENE, AND CYMENE.

By H. D. LAW, and F. MOLLWO PERKIN.

INTRODUCTION.

IN continuation of the work upon the electrolytic oxidation of the hydrocarbons of the benzene series, we have now studied the oxidation of hydrocarbons containing groups other than methyl, or compounds which contain the methyl group and another group, as for example cymene, in which there is a methyl and isopropyl group in the same nucleus.

In our first communication upon the oxidation of substances containing the methyl group (*Trans. Faraday Soc.*, Jan., 1905, i., p. 31) it was shown that in all cases the methyl group was oxidised mainly to the aldehyde, or second stage of oxidation, and where there was more than one methyl group in the nucleus that chiefly the mono-aldehyde was produced, and attention was drawn to the comparative stability of the aldehyde group to electrolytic oxidation, because in no case was the corresponding acid obtained. A small quantity of a substance, which did not react with sodium bisulphite, and was, therefore, not an aldehyde, was also obtained. This substance we have since proved to be the corresponding alcohol.



In the present instance, as is the case with toluene, the xylenes, and mesitylenes, the most satisfactory method of oxidation has been to dissolve the hydrocarbon in an excess of acetone, and add the mixture to the electrolyte, the bulk of which was usually rather less than the bulk of the acetone added. For example, a good mixture is 300 to 400 c.c. of acetone and 200 c.c. of 5 to 10 per cent sulphuric acid.

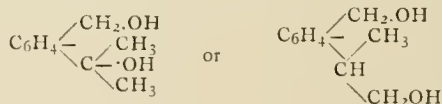
In the paper just referred to (*loc. cit.*) we drew attention to the difficulty experienced owing to the continual increase in concentration of the anode solution by the transference of the SO_4^{2-} ions to this compartment when the electric current was passed. As for 50 grms. of hydrocarbon about 70 ampere hours of current are required to be used, it follows that towards the end of the operation the sulphuric acid concentration becomes very considerable. We were of the opinion that this high concentration and the fact that an aldehyde and acetone were present, would probably

tend to cause condensation and increase the quantity of unworkable tarry product always obtained in greater or less quantities. In a paper shortly to be published, it will be shown that by working without a diaphragm in the case of toluene, it has been found possible to increase the yield of benzaldehyde obtained from about 8 per cent to 18 or 20 per cent. The apparatus which was employed and found satisfactory is shown in the accompanying illustration. It consists of a circular glass vessel capable of holding about 750 c.c. The jar is closed by means of a large cork, through the centre of which passes a glass stirrer. Two anodes of sheet platinum, having together a total surface of 1.5 sq. d.cm., are placed at opposite sides of the vessel, and in between them and opposite to each other, two cathodes of stout platinum wire, which have the form of loose spirals. The total area of the cathodes was usually about 20–25 sq. c.m. By employing this large anode surface and small cathode surface, the oxidation is very complete and the reduction is practically nil. The amount of alcohol found is about the same as when a porous cell is used; therefore, the alcohol is an oxidation product and is not formed by the reduction of the aldehyde. We have also reduced the strength of the sulphuric acid employed as the electrolyte from about 10 to 5 per cent. As in the previous case when dealing with hydrocarbons containing the methyl group, we have invariably obtained an aldehyde and also an alcohol, but the oxidation has never gone so far as to produce the corresponding acid.

With ethyl benzene, the secondary alcohol $\text{C}_6\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{CH}_3$ was obtained in considerable quantity, and also a small quantity of what was probably the primary alcohol $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\text{OH}$, but this was not obtained in a state of sufficient purity to give good analytical numbers. Benzaldehyde was also obtained, but only after the bulk of the hydrocarbon had been converted into the alcohol. It is interesting to compare this oxidation with the products obtained by purely chemical methods.

When oxidised with chromic and sulphuric acids, or with nitric acid, ethyl benzene yields benzoic acid. But on oxidation with chromic acid, dissolved in acetic acid, acetophenone is said to be produced. It might have been supposed that in our case, on further oxidation, the secondary alcohol would have yielded acetophenone, but we were unable to find any.

Cymene (*p*-methylisopropylbenzene) yielded about 20 per cent of a mixture of alcohols and about 10 per cent of an aldehyde. On analysis, the alcohol boiling-point $235\text{--}240^\circ$, which occurred in the largest proportion, was found to be a dihydric-alcohol, and may be either—



The lower fraction $215\text{--}220^\circ$ is a mixture of a mono- and a dihydric-alcohol.

The aldehyde obtained is $\text{C}_6\text{H}_4\cdot\text{CHO}$, showing that the methyl group is more readily attacked than the isopropyl group. When cymene is oxidised with potassium permanganate hydroxyisopropylbenzoic acid, $\text{OH}\cdot\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_4\cdot\text{COOH}$, is produced, which on further oxidation is converted into terephthalic acid. Cold nitric acid yields *p*-methyl tolyl ketone, but the hot acid gives *p*-toluic acid, in this last case the isopropyl group being attacked before the methyl. Cumene (*isopropylbenzene*), on oxidation with chromic acid, gives benzoic acid. But with chromyl chloride acetophenone and hydratopaldehyde we find that electrolytic oxidation yields an aldehyde, boiling-point $220\text{--}225^\circ$, and a small quantity of a di- and monohydric-alcohol. On one occasion benzaldehyde was obtained. Owing to the cumene which we had not being pure and apparently consisting of a mixture of cumene and other hydrocarbons, the results obtained were not so satis-

* Read before the Faraday Society, July 3, 1905.

factory as we would have liked. We hope, therefore, on a future occasion to examine this substance further.

EXPERIMENTAL.

Ethylbenzene.

The ethylbenzene which we employed was prepared synthetically by the action of sodium upon a mixture of bromobenzene and ethyl iodide.

Two quantities of 50 grms. each were subjected to oxidation. The ethylbenzene was dissolved in 400 c.c. of acetone, and added to 200 c.c. of 10 per cent sulphuric acid and placed in the electrolysis vessel just described. The whole apparatus was placed in a vessel through which cold water was caused to circulate. Before commencing the electrolysis the mixture was brought into an homogeneous emulsion by means of the stirrer, and the stirring continued during the whole operation.

Anode surface	150 sq. c.m.
Cathode surface	25 sq. c.m.
Current	2 ampères.
E.M.F.	5-6 volts.
Temperature	18°

The anode C.D. was therefore 1.3 ampères per sq. d.cm. of surface.

The current was passed for 40 hours, so that 80 ampère hours of current was employed. This is about one-third less than the theoretical amount of current required according to Equation IV. (*prox.*) to convert the whole of the hydrocarbon into benzaldehyde. The acetone was now distilled off and the dark oily product subjected to steam distillation. The light yellow oily distillate was separated from the aqueous layer, which was then extracted with ether. The ethereal solution was mixed with the oil, and then an excess of a saturated solution of sodium bisulphite added. After standing for 24 hours the bisulphite compound was filtered off. On decomposing this a small quantity of an aldehyde, which boiled at 180°, was obtained. This is the boiling-point of benzaldehyde, and its identity was further proved by exposing it to the air when it became oxidised to benzoic acid m.p. 119°. The yield of benzaldehyde was 3 grms., that is 6 per cent.

The ethereal solution obtained after filtering off the bisulphite compound was washed with water and sodium carbonate and dried over anhydrous sodium sulphate. The ether was distilled off, and on distilling the following fractions were obtained:—

I. 100-170° 8 grms.	} from 100 grms. of ethylbenzene.
II. 170-206° 16 grms.	
III. 206-220° 2 grms.	
Residue about 1 grm.	

The lowest fraction was mainly unchanged ethylbenzene and was not further examined. Fraction II., which on re-distillation almost all passed over between 200-202°, was analysed.

Substance = 0.1130, $H_2CO_2 = 0.3240$, $H_2O = 0.0804$:—

Found.	Calculated for $C_8H_{10}O$.
C = 78.21	C = 78.68
H = 7.91	H = 8.20

These numbers and the boiling-point show the substance to be the secondary alcohol phenyl methyl carbinol, $C_6H_5 \cdot CH(OH)CH_3$, the boiling-point of which is given in the literature as 202-204°.

There was only a very small quantity of the higher fraction No. III. after re-fractionation which boiled at 210°, and this, therefore, was not analysed. Its boiling-point, however, shows it to be the primary alcohol phenyl ethyl alcohol, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot OH$, whose boiling-point is 212°, the same as found by us.

In a second oxidation no aldehyde was obtained, only the alcohols being produced. In this case there was also a

small quantity of unchanged ethyl benzene, the oxidation having been interrupted before the whole of it had been attacked. There was always a very considerable quantity of tarry products obtained.

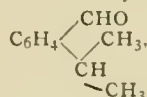
Cymene.

The oxidation of this product was carried out in exactly the same manner as that of the ethyl benzene. The current conditions being:—

Anode surface, 150 sq. c.m.
Cathode surface, 20 sq. c.m.
Current density at anode, 1.25 amperes per sq. d.cm.
E.M.F.

In all 200 grms. of cymene was subjected to oxidation, 50 grms. being oxidised in each experiment. The products of oxidation were worked up together. The excess of acid was neutralised with sodium carbonate and the acetone distilled off, the residue being subjected to steam distillation. The distillate after shaking out with ether was then treated with sodium bisulphite. In order that the whole of the aldehyde should be converted into the bisulphite compound, it was found advisable to allow the mixture to stand in contact with the sodium bisulphite for at least a week.

The bisulphite compound was filtered off, decomposed with sodium carbonate, and the aldehyde steam distilled; the distillate extracted with ether, which after drying with calcium chloride was distilled off and the fragrant-smelling aldehyde distilled. It almost all passed over at 235-237°. This shows it to be cumene aldehyde—



the boiling-point of which is 236.5°. It therefore follows that the oxidation as far as aldehyde formation is concerned only took place in the methyl group. In order to further prove that this substance is cuminaldehyde, a small quantity was exposed to the air for some days. By this means it was converted into the acid which, after re-crystallising from acetone and acetic acid, melted at 116°, showing it to be cumic acid, the melting point of which is given as 116° in the literature.

Carbazone.

This substance, which has not previously been prepared, was made in the usual manner. It is moderately soluble in absolute alcohol, from which it crystallised in shining pearly plates, m. p. 206-208°, with decomposition. A nitrogen determination was made, when the following numbers were obtained:—

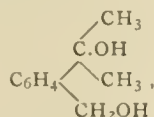
Substance 0.1046, Bar. = 754 m.m., $t = 24^\circ$, $N = 19.6$ c.c.

Found.	Calculated for $C_{11}H_{15}N_3O$.
N = 20.84	= 20.49

The portion which did not react with sodium bisulphite, and which consisted of 40 grms., was distilled, when the following fractions were obtained: I. 200-240°, II. 240-280°.

On refractionation two fractions were obtained: I. 210-215°, II. 222-224°.

The analysis of the higher fraction showed it to consist of a di-alcohol, probably—



but as these di-alcohols do not appear to be known, we are at present unable to decide which it is.

Substance = 0.1360, CO₂ = 0.3580, H₂O = 0.1010.

Found.	Calculated for C ₁₀ H ₁₄ O ₂ .
C = 71.79	C = 72.29
H = 8.25	H = 8.42

It was not found possible to obtain satisfactory numbers for the lower fraction, but it undoubtedly consists of a mixture of the mono- and di-alcohols, as the following numbers show :—

Substance = 0.1070, CO₂ = 0.3016, H₂O = 0.0880.

Found.	Calculated for C ₁₀ H ₁₄ O.
C 76.87	C = 80.00
H = 9.13	H = 9.33

Cumene.

There was considerable difficulty in obtaining pure cumene. The product we finally used was obtained from Kahlbaum, and it boiled at 160—170°. This was repeatedly shaken out with small quantities of strong sulphuric acid until the acid ceased to be coloured. On steam distillation and subsequent fractionation it all passed over between 155° and 158°. Pure cumene, according to the literature, should boil at 153°. The results of our work show, however, that the bulk of this product did actually consist of cumene. 150 grms. of the cumene thus purified were mixed with 350 c.c. acetone and 200 c.c. of 5 per cent sulphuric acid and electrolysed for forty-eight hours. This is equivalent to 120 ampère hours, whereas theoretically 90 ampère hours are required to convert one of the methyl groups into an aldehyde.

Current = 2.5 ampères.

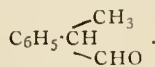
C.D. = 1.66 ampères per sq. d.cm.

E.M.F. = 2.5—4 volts.

Temperature = 18—20°.

At the end of the time the acetone was distilled off, and the dark brown oily residue steam distilled. The distillate was extracted with ether, and treated with sodium bisulphite. At the end of twelve hours scarcely any bisulphite compound had formed, so it was allowed to stand altogether for a week, when a considerable amount had formed (8 grms. of dry product, corresponding to 4.5 grms. of aldehyde). The amount of unchanged cumene recovered was 75 grms. and about 4 grms. of an alcohol substance, the rest of the cumene having been converted into a resinous substance. The large amount of cumene recovered and the small amount of oxidation products obtained show that the isopropyl group is not all readily attacked by electrolytic oxidation.

The aldehyde obtained from the bisulphite compound was fractionated. In the first place two fractions boiling at 200—220° and 220—225° were obtained. On refractionation less than 1 gm. came over below 220°, the rest boiling between 220° and 225°. Analysis showed that the aldehyde was evidently a mixture of cuminaldehyde and hydratrop-aldehyde—



The remainder of the aldehyde was therefore dissolved in alcohol, and treated with semicarbazine hydrochloride and sodium acetate, whereby it was converted into a carbazone. The carbazone was found to consist of two substances, one of which was only soluble in absolute alcohol with difficulty, but the other was fairly soluble. Owing to their different solubilities a separation was effected by crystallisation from absolute alcohol. The portion which dissolved with difficulty separated out in the form of fine sandy crystals. The melting-point was not very definite, as after three crystallisations the substance melted at between 216° and 221°. The other substance was evidently the carbazone of cumenic aldehyde, but it was not obtained quite pure, and melted at 194—202° (the carbazone of cumenic aldehyde melts at 206—208°).

A nitrogen analysis gave the following numbers :—

Substance = 0.1613, Bar. = 758, *t* = 28, *N* = 32.5 c.c.

Found.	Theory for C ₁₀ H ₁₃ N ₃ O.
<i>N</i> = 22.06	<i>N</i> = 21.99

On one occasion, when the amount of current passed was considerably more than that theoretically necessary, a mixture of this aldehyde and benzaldehyde was obtained, the presence of benzaldehyde being proved by obtaining benzoic acid.

The alcoholic portions from several experiments, amounting in all to about 7 grms., were carefully distilled, when fractions boiling at 215—220° and 235—240° were obtained. Owing to the small quantity we had to deal with, it was not possible to refractionate our products. They were therefore analysed separately, and although good analytical numbers could hardly be expected, the numbers obtained showed that the lower fraction was a practically pure monohydric-alcohol and the higher fraction a mixture of the dihydric-alcohol and monohydric-alcohol.

Analysis of lower fraction 215—220° :—

Substance = 0.110, CO₂ = 0.3190, H₂O = 0.0855.

Found.	Calculated for C ₉ H ₁₂ O.
C = 79.09	C = 79.41
H = 8.63	H = 8.82

Analysis of higher fraction 235—240° :—

Substance = 0.1100, CO₂ = 0.3070, H₂O = 0.0776.

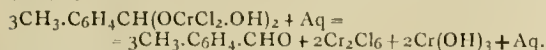
Found.	Calculated for C ₉ H ₁₂ O ₂ .
C = 76.12	C = 71.05
H = 7.84	H = 7.95

As these alcohols do not appear to be known, we are unable to say whether the monohydric-alcohol obtained by us was the primary or tertiary alcohol. In all probability, however, as we have obtained an aldehyde, the alcohol is the primary alcohol, and the dihydric-alcohol is probably the dihydric-primary alcohol.

DISCUSSION OF RESULTS.

In connection with the electrolytic oxidation of substituted hydrocarbons of the benzene series, several very interesting facts have been brought out. The oxidation in acid solution is much less violent than is usually supposed, and certain groups which are extremely readily attacked by even the mildest of ordinary oxidising agents, such as the aldehyde group, are relatively stable when acted upon electrolytically. Thus when oxidising toluene or the xylenes, it was found that the methyl group was oxidised to the alcohol and then to the aldehyde, but that so long as there was any unchanged hydrocarbon present the aldehyde group was apparently unacted upon. Furthermore, that in the case of the xylenes one CH₃ group was invariably attacked before the other, and that until practically the whole of the xylene had been converted into the monohydric-alcohol, or aldehyde, the second CH₃ group was not attacked; the same is the case with the mesitylenes. The cause of this is probably to be traced to the protective action of the —CH₂OH or —CHO groups, both of which are more negative in character than the original —CH₃ group. The protective action of a negative group is strikingly shown when it is endeavoured to oxidise the cresols or the nitrotoluenes, the oxidation of these substances being extremely difficult, especially by electrolytic means. This characteristic has also been brought out in the oxidation of cymene, where the aldehyde C₇H₇.C₆H₄.CHO is the main product, the methyl group being first attacked and preventing further action upon the isopropyl group. In isopropyl the hydrogen atom in the tertiary position is usually considered the most readily attacked by oxidising agents. But to judge from the results obtained on oxidising cymene and cumene, the hydrogen atoms in the methyl group are more readily attacked when electrolytic methods of oxidation are employed.

In what manner, then, does electrolytic oxidation take place? When hydrocarbons are oxidised by chemical methods, the alcohol is rarely produced,* and the aldehyde only when CrO_2Cl_2 is employed as oxidising agent. In this latter case, the first action is the formation of an unstable combination between the chromyl chloride and one of the methyl groups of the xylene. For example, $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3 + 2\text{O}_2\cdot\text{CrCl}_2 = \text{C}_6\text{H}_3\cdot\text{CH}_4\text{CH}(\text{OCrCl}_2\cdot\text{OH})_2$. This is then decomposed by water with formation of the aldehyde, so that we may consider this a case of hydrolytic oxidation.



From our results it appears that in electrolytic oxidation, carried out in dilute acid or alkaline solutions, the hydroxyl group is the oxidising agent, and not oxygen.

In solutions containing sulphuric acid or other substances, such as potassium sulphate, there are beside SO_4 ions also OH' ions.

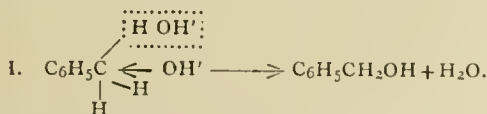
But according to the law of mass action, the product of the concentrations of the hydrogen and hydroxyl ions is always constant, and is independent of the other substances which may be present. Now the transport velocity of the OH' ions is far greater than that of the SO_4 ions, therefore there will be a tendency for them to group round the anode; they will therefore rather be discharged than the SO_4 ions.

According to Le Blanc, in the electrolysis of water a primary decomposition takes place. The actual electrolysis—i.e., the conductivity—is brought about by all the ions in the solution, but at the electrode that action takes place which proceeds most easily; this is the separation of the hydroxyl and hydrogen ions. We consider that the results of our work bear out Le Blanc's assumption that, provided the current is not too strong, the electrolysis of water is a primary reaction. We have worked throughout with fairly low currents, never exceeding and rarely reaching a greater density than 1.5 ampères per square decimetre of anode surface.

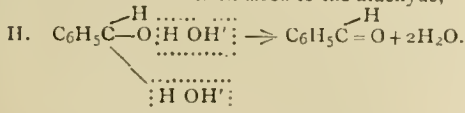
Where it is desired to form products by the action or union of ions other than hydroxyl, it is always necessary to have high concentration of the solute, and equally important to employ a high current density at the anode. Thus, in the formation of persulphuric acid or of chlorates or hypochlorites, strong solutions and very high current densities are always found necessary.

The current employed by us was too high for the reaction to be entirely primary, and this probably accounts for the fact that considerably more than the theoretical amount of current was required to complete the oxidation. Furthermore, we are not prepared to say that no part of the oxidation is due to oxygen liberated at the anode.

Assuming the oxidations to be produced by the action of the hydroxyl group, the following equations will explain the reactions which take place. With toluene and the xylenes the primary alcohol is first formed thus:—



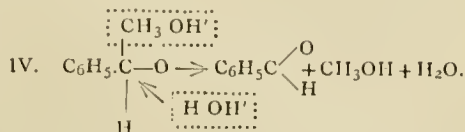
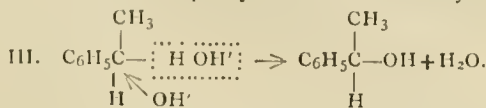
The alcohol is then further oxidised to the aldehyde,—



With ethylbenzene it is mainly the hydrogen attached at the β -position which is attacked, therefore no aldehyde is

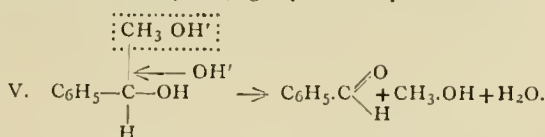
* When cymene is oxidised with potassium permanganate, $\text{OH}\cdot\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{COOH}$ is produced (*Ber.*, xiv., 484). In this case the alcohol is produced owing to the hydrogen atom in the tertiary position being attacked, a tertiary alcohol being the only possible product.

obtained; further oxidation could only produce acetophenone, which, however, we have not obtained, although a portion has been completely oxidised to benzaldehyde.



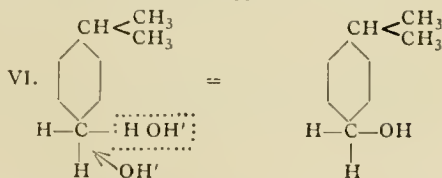
We have not found methyl alcohol in our solutions, and supposing it is produced it would be a very difficult matter to show its presence in a mixture containing such a large amount of acetone as was employed to dissolve the ethylbenzene. If, however, one OH unites with the H of the alcoholic group, the oxygen would now unite with the carbon by a double bond, and the CH_3 would be forced off, and might at the same time unite with an hydroxyl.

Or this, by supposing the OH' ion on discharge to unite with the CH_3 group, which then being overloaded breaks off, and another hydroxyl group takes its place. We now



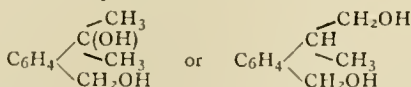
have two hydroxyls attached to one atom, and, as is well known, the tendency is under such conditions for water to be split off, with the result that an aldehyde is produced. The same explanation may be used to explain the aldehyde formation in II. and VIII.

Turning to cymene, we have a comparatively simple case, the first group acted upon being the methyl group. For this the Equation I. for toluene applies:—



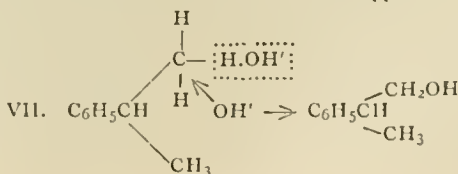
This is then further oxidised to cuminaldehyde, for which which we need not write the equation.

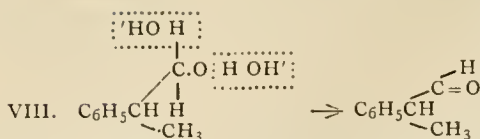
We are not able at present to say whether the dihydric alcohol obtained by us is—



The fact of cumene forming the primary alcohol, which is proved by the formation of an aldehyde, goes to show that in all probability the dihydric alcohol in the case of cumene is the dihydric-primary alcohol. This is a matter which we hope to clear up on subsequent investigation.

In the case of cumene the main reaction appears to be—





The dihydric-alcohol being formed by a similar oxidation of the second methyl group. Or it may be by oxidation of the tertiary hydrogen atom.

With reference to cumene, a little consideration shows that it is not a matter for surprise that the isopropyl group is not readily attacked. Genvresse (*Bull. Soc. Chim.*, 1893, [3], ix., 219) has shown that when normal propylbenzene is acted upon by chlorine at boiling temperature, the halogen enters the side chain. When, however, isopropylbenzene is treated in the same manner, the chlorine enters the nucleus. We hope to be shortly in a position to try further experiments with both normal propyl and isopropylbenzene.

Renard (*Comptes Rendus*, xci., 175) states that on electrolysis a mixture of benzene, sulphuric acid, and alcohol, he obtained phenose, $\text{C}_6\text{H}_6(\text{OH})_6$. Although several attempts have been made in this laboratory to prepare phenose by this means, we have not so far been successful. The assumption of hydroxylic oxidation makes it quite probable that such a substance might be obtained by oxidising benzene electrolytically. It should be quite possible, given the right conditions, to add two, four, or six hydroxyl groups to benzene. But considering the impossibility of obtaining hexahydrobenzene by actual reduction of benzene, it is not probable that the reaction would be an easy one to carry out.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 2, July 10, 1905.

Comparison of Properties of various Steels.—Léon Guillet.—The author's researches on certain steels which are alloys of iron, carbon, and a third substance show that a micrographical observation of such steels lead to an extremely interesting conclusion, both from the point of view of the commercial use of the steels, and even of their composition. The single case of perlitic steel still remains doubtful.

Hydrated Ferric Sulphate: Molecular Transformations.—A. Recoura.—The author finds that when a solution of ferric sulphate is left to evaporate, the solidification takes place in two phases. When the liquor has acquired a sufficient concentration the basic sulphate, $6[\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3] \cdot \text{Fe}_2\text{O}_3$, separates out, after which the acid liquid combines with the basic sulphate, and a yellow solid product is obtained of composition $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 9\text{H}_2\text{O}$. The yellow sulphate behaves as a very unstable compound of the basic and acid sulphates. The white sulphate is much more stable.

A Dextro-dilactide.—E. Jungfleisch.—The author's investigations on dilactides show that the dilactide (*d l*) is only formed after prolonged action of heat, the *d*-lactic acid changing very gradually into the inactive derivative by compensation, and so conforming to the general rule. By reducing to a minimum the time of distillation, it is possible to obtain the *d*-dilactide. This substance gives on analysis and cryoscopic examination results showing it to have the formula $\text{C}_6\text{H}_8\text{O}_4$.

Hydrogenation of Ketoximes. Synthesis of New Amines.—A. Mailhe.—By direct hydrogenation of the

oximes by the use of finely-divided metals, such as nickel and copper, the primary and secondary amines are formed with good yield. The formation of the secondary amines proves the reduction of the ketoximes—that is to say, those compounds in which the remaining NH is united to a secondary term, CH—substances generally very difficult to prepare. Except for di-isopropylamine, they were hitherto altogether unknown, but by the present method of direct hydrogenation of the ketoximes in presence of finely-divided nickel and copper they are easily prepared.

Synthesis of a New Leucine.—L. Bouveault and René Locquin.—The authors obtain the best results by the hydrogenation of their oximide ether by means of sodium in cold alcoholic solution, the neutrality of the solution being maintained by continual additions of alcohol saturated with hydrochloric acid gas. They thus prepare, with a yield of about 60 per cent, α -amino-butyl acetate of ethyl—the ethylic ether of the required leucine. It is a colourless liquid with a disagreeable smell, boiling at $90-92^\circ$ under a pressure of 15 mm.

Sparteïn: Symmetric Character of the Molecule.—Charles Moureu and Amand Valeur.—The authors perform a series of experiments on sparteïn to prove that the positions occupied by the two atoms of nitrogen are symmetrical with regard to one another.

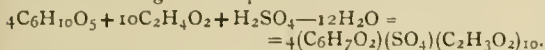
Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxviii., No. 8, 1905.

Synthesis of Hydrazoic Acid.—Arthur Wesley Browne.—The author has synthesised hydrazoic acid by dissolving hydrazine sulphate in water, adding sulphuric acid and hydrogen peroxide, and heating to a moderately high temperature in a distilling flask. It was found that the presence of a considerable excess of hydrogen peroxide reduced the yield, while more hydrazoic acid was formed as the amount of sulphuric acid present in the solution was increased up to a certain limit. The equation $3\text{N}_2\text{H}_4 + 5\text{H}_2\text{O}_2 = 2\text{HN}_3 + 10\text{H}_2\text{O}$ appears to represent most simply and correctly the reaction which occurs. The maximum yield obtained was about 28 per cent of the theoretical, and this method is of interest as being the first in which hydrazine is converted into hydrazoic acid in the absence of any other substance containing nitrogen. Other experiments show that small quantities of hydrazoic acid can be prepared by the action of certain other oxidation agents besides hydrogen peroxide upon hydrazine sulphate.

Quantitative Determination of Lead by Persulphates in Acid Solution.—M. Dittrich and A. Reise.—If a 10 per cent solution of pure ammonium persulphate is added to a solution of lead nitrate a white crystalline precipitate of lead sulphate is at first formed, but rapidly darkens, owing to the formation of the peroxide. After five hours the precipitate may be washed with dilute ammonium sulphate without any trace of lead going into solution, and on being ignited with addition of a drop of sulphuric acid it goes quantitatively into sulphate. This method of precipitation is far more convenient than the ordinary method with sulphuric acid and alcohol. The solution need not stand so long, and, moreover, the lengthy processes of washing with alcohol and expelling the latter are avoided. The precipitation and conversion into PbO_2 are greatly accelerated if some silver nitrate is present in the lead solution, filtration being then possible after heating to 80° on the water-bath for three hours. On addition of hydrochloric acid to the precipitate chlorine is evolved, and in the solution obtained only traces of sulphate are to be detected; it is, however, not possible to convert all the precipitate into peroxide, even on heating and adding more persulphate. Apparently a silver peroxide is formed which very readily gives up oxygen for the oxidation of the lead, and at once takes up more oxygen from the persulphate.

Aceto-sulphates of Cellulose.—C. F. Cross. E. J. Bevan, and J. F. Briggs.—By the action of glacial acetic

acid, acetic anhydride, and sulphuric acid upon cellulose a neutral ester cellulose aceto-sulphate is formed. This compound is characterised by the resistance of the SO_4 residue towards alkaline saponification agents, while it is exceedingly readily hydrated. The substance when dried in air contains 8 per cent of hygroscopic moisture, and thus forms an important exception to the general rule which holds good for other series of cellulose esters. By altering the proportion of H_2SO_4 to the acetic acid anhydride mixture, instead of the normal cellulose, aceto-sulphate products soluble in water are obtained; these contain a higher percentage of combined SO_4 than the insoluble product. The soluble esters show well-defined colloid properties; they can be salted out from the solution, and thus separated as gelatinous precipitates. The normal ester is soluble in dilute alcohol. From quantitative saponification experiments it is found that the esters are formed according to the equation—



Thus the proportion $4\text{C}_6\text{H}_{10}\text{O}_5 : \text{H}_2\text{SO}_4$ shows that cellulose in its reactions must behave like a complex with at least 24 carbon atoms. Even when combined with a dibasic acid, the cellulose complex retains unimpaired its character of a homogeneous compound; the authors' researches do not show that a selective molecular action takes place, or a splitting up of the original cellulose aggregate.

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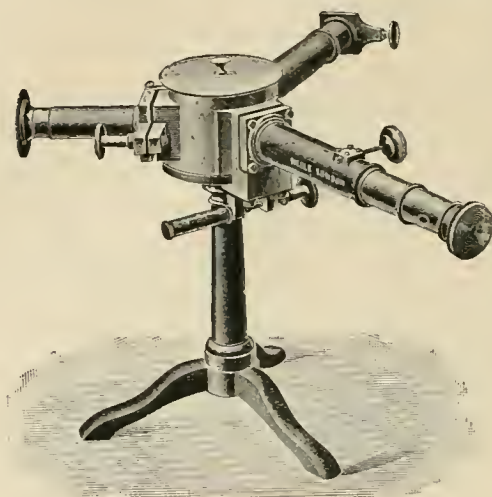
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THE CHEMICAL NEWS.

VOL. XCII., No. 2385.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

SOUTH AFRICA, 1905.

FIRST PART OF ADDRESS OF THE PRESIDENT,
Professor G. H. DARWIN, M.A., LL.D., Ph.D., F.R.S.
(Delivered at CAPE TOWN, August 15th).

BARTHOLOMEU DIAZ, the discoverer of the Cape of Storms, spent sixteen months on his voyage, and the little flotilla of Vasco de Gama, sailing from Lisbon on July 8, 1497, only reached the Cape in the middle of November. These bold men, sailing in their puny fishing smacks to unknown lands, met the perils of the sea and the attacks of savages with equal courage. How great was the danger of such a voyage may be gathered from the fact that less than half the men who sailed with de Gama lived to return to Lisbon. Four hundred and eight years have passed since that voyage, and a ship of 13,000 tons has just brought us here, in safety and luxury, in but little more than a fortnight!

How striking are the contrasts presented by these events! On the one hand, compare the courage, the endurance, and the persistence of the early navigators with the little that has been demanded of us; on the other hand, consider how much man's power over the forces of Nature has been augmented during the past four centuries. The capacity for heroism is probably undiminished, but certainly the occasions are now rarer when it is demanded of us. If we are heroes, at least but few of us ever find it out, and, when we read stories of ancient feats of courage, it is hard to prevent an uneasy thought that, notwithstanding our boasted mechanical inventions, we are perhaps degenerate descendants of our great predecessors.

Yet the thought that to-day is less romantic and less heroic than yesterday has its consolation, for it means that the lot of man is easier than it was. Mankind, indeed, may be justly proud that this improvement has been due to the successive efforts of each generation to add to the heritage of knowledge handed down to it by its predecessors, whereby we have been born to the accumulated endowment of centuries of genius and labour.

I am told that in the United States the phrase "I want to know" has lost the simple meaning implied by the words, and has become a mere exclamation of surprise. Such a conventional expression could hardly have gained currency except amongst a people who aspire to knowledge. The dominance of the European race in America, Australasia, and South Africa has no doubt arisen from many causes, but amongst these perhaps the chief one is that not only do "we want to know," but also that we are determined to find out. And now within the last quarter of a century we have welcomed into the ranks of those who "want to know" an oriental race, which has already proved itself strong in the peaceful arts of knowledge.

I take it, then, that you have invited us because you want to know what is worth knowing; and we are here because we want to know you, to learn what you have to tell us, and to see that South Africa of which we have heard so much.

The hospitality which you are offering us is so lavish, and the journeys which you have organised are so extensive, that the cynical observer might be tempted to describe our meeting as the largest picnic on record. Although we

intend to enjoy our picnic with all our hearts, yet I should like to tell the cynic, if he is here, that perhaps the most important object of these conferences is the opportunity they afford for personal intercourse between men of like minds who live at the remotest corners of the earth.

We shall pass through your land with the speed and the voracity of a flight of locusts; but, unlike the locust, we shall, I hope, leave behind us permanent fertilisation in the form of stimulated scientific and educational activity. And this result will ensue whether or not we who have come from Europe are able worthily to sustain the lofty part of prophets of science. We shall try our best to play to your satisfaction on the great stage upon which you call on us to act, and if when we are gone you shall, amongst yourselves, pronounce the performance a poor one, yet the fact will remain, that the meeting has embodied in a material form the desire that the progress of this great continent shall not be merely material; and such an aspiration secures its own fulfilment. However small may be the tangible results of our meeting, we shall always be proud to have been associated with you in your efforts for the advancement of science.

We do not know whether the last hundred years will be regarded for ever as the *sacculum mirabile* of discovery, or whether it is but the prelude to yet more marvellous centuries. To us living men, who scarcely pass a year of our lives without witnessing some new marvel of discovery or invention, the rate at which the development of knowledge proceeds is truly astonishing; but from a wider point of view the scale of time is relatively unimportant, for the universe is leisurely in its procedure. Whether the changes which we witness be fast or slow, they form a part of a long sequence of events which begin in some past of immeasurable remoteness, and tend to some end which we cannot foresee. It must always be profoundly interesting to the mind of man to trace successive cause and effect in the chain of events which make up the history of the earth and all that lives on it, and to speculate on the origin and future fate of animals, and of planets, suns, and stars. I shall try, then, to set forth in my Address some of the attempts which have been made to formulate evolutionary speculation. This choice of a subject has, moreover, been almost forced on me by the scope of my own scientific work, and it is, I think, justified by the name which I bear. It will be my fault and your misfortune if I fail to convey to you some part of the interest which is naturally inherent in such researches.

The man who propounds a theory of evolution is attempting to re-construct the history of the past by means of the circumstantial evidence afforded by the present. The historian of man, on the other hand, has the advantage over the evolutionist in that he has the written records of the past on which to rely. The discrimination of the truth from amongst discordant records is frequently a work demanding the highest qualities of judgment; yet when this end is attained it remains for the historian to convert the arid skeleton of facts into a living whole by clothing it with the flesh of human motives and impulses. For this part of his task he needs much of that power of entering into the spirit of other men's lives which goes to the making of a poet. Thus the historian should possess not only the patience of the man of science in the analysis of facts, but also the imagination of the poet to grasp what the facts have meant. Such a combination is rarely to be found in equal perfection on both sides, and it would not be hard to analyse the works of great historians so as to see which quality was predominant in each of them.

The evolutionist is spared the surpassing difficulty of the human element, yet he also needs imagination, although of a different character from that of the historian. In its lowest form his imagination is that of the detective who re-constructs the story of a crime; in its highest it demands the power of breaking loose from all the trammels of convention and education, and of imagining something which has never occurred to the mind of man before. In every case the evolutionist must form a theory for the facts before

him, and the great theorist is only to be distinguished from the fantastic fool by the sobriety of his judgment—a distinction, however, sufficient to make one rare and the other only too common.

The test of a scientific theory lies in the number of facts which it groups into a connected whole; it ought besides to be fruitful in pointing the way to the discovery and co-ordination of new and previously unsuspected facts. Thus a good theory is in effect a cyclopædia of knowledge, susceptible of indefinite extension by the addition of supplementary volumes.

Hardly any theory is all true, and many are not all false. A theory may be essentially at fault, and yet point the way to truth, and so justify its temporary existence. We should not, therefore, totally reject one or other of two rival theories on the ground that they seem, with our present knowledge, mutually inconsistent, for it is likely that both may contain important elements of truth. The theories of which I shall have to speak hereafter may often appear discordant with one another according to our present lights. Yet we must not scruple to pursue the several divergent lines of thought to their logical conclusions, relying on future discovery to eliminate the false and to reconcile together the truths which form part of each of them.

In the mouths of the unscientific evolution is often spoken of as almost synonymous with the evolution of the various species of animals on the earth, and this again is sometimes thought to be practically the same thing as the theory of Natural Selection. Of course those who are conversant with the history of scientific ideas are aware that a belief in the gradual and orderly transformation of Nature, both animate and inanimate, is of great antiquity.

We may liken the facts on which theories of evolution are based to a confused heap of beads, from which a keen-sighted searcher after truth picks out and strings together a few which happen to catch his eye, as possessing certain resemblances. Until recently, theories of evolution in both realms of Nature were partial and discontinuous, and the chains of facts were correspondingly short and disconnected. At length the theory of Natural Selection, by formulating the cause of the divergence of forms in the organic world from the parental stock, furnished the naturalist with a clue by which he examined the disordered mass of facts before him, and he was thus enabled to go far in deducing order where chaos had ruled before, but the problem of reducing the heap to perfect order will probably baffle the ingenuity of the investigator for ever.

So illuminating has been this new idea that, as the whole of Nature has gradually been re-examined by its aid, thousands of new facts have been brought to light, and have been strung in due order on the necklace of knowledge. Indeed, the transformation resulting from the new point of view has been so far-reaching as almost to justify the misapprehension of the unscientific as to the date when the doctrines of evolution first originated in the mind of man.

It is not my object, nor indeed am I competent, to examine the extent to which the theory of Natural Selection has needed modification since it was first formulated by my father and Wallace. But I am surely justified in maintaining that the general principle holds its place firmly as a permanent acquisition to modes of thought.

Evolutionary doctrines concerning inanimate Nature, although of much older date than those which concern life, have been profoundly affected by the great impulse of which I have spoken. It has thus come about that the origin and history of the chemical elements and of stellar systems now occupy a far larger space in the scientific mind than was formerly the case. The subject which I shall discuss to-night is the extent to which ideas, parallel to those which have done so much towards elucidating the problems of life, hold good also in the world of matter; and I believe that it will be possible to show that in this respect there exists a resemblance between the two realms of Nature, which is not merely fanciful. It is proper

to add that as long ago as 1873 Baron Karl du Prel discussed the same subject from a similar point of view, in a book entitled "The Struggle for Life in the Heavens" ("Der Kampf um's Dasein am Himmel," zweite Auflage, Denicke, Berlin, 1876).

Although inanimate matter moves under the action of forces which are incomparably simpler than those governing living beings, yet the problems of the physicist and the astronomer are scarcely less complex than those which present themselves to the biologist. The mystery of life remains as impenetrable as ever, and in his evolutionary speculations the biologist does not attempt to explain life itself, but, adopting as his unit the animal as a whole, discusses its relationships to other animals and to the surrounding conditions. The physicist, on the other hand, is irresistibly impelled to form theories as to the intimate constitution of the ultimate parts of matter, and he desires further to piece together the past histories and the future fates of planets, stars, and nebulae. If then the speculations of the physicist seem in some respects less advanced than those of the biologist, it is chiefly because he is more ambitious in his aims. Physicists and astronomers have not yet found their Johannesburg or Kimberley; but, although we are still mere prospectors, I am proposing to show you some of the dust and diamonds which we have already extracted from our surface mines.

The fundamental idea in the theory of Natural Selection is the persistence of those types of life which are adapted to their surrounding conditions, and the elimination by extermination of ill-adapted types. The struggle for life amongst forms possessing a greater or less degree of adaptation to slowly varying conditions is held to explain the gradual transmutation of species. Although a different phraseology is used when we speak of the physical world, yet the idea is essentially the same.

The point of view from which I wish you to consider the phenomena of the world of matter may be best explained if, in the first instance, I refer to political institutions, because we all understand, or fancy we understand, something of politics, whilst the problems of physics are commonly far less familiar to us. This illustration will have a further advantage in that it will not be a mere parable, but will involve the fundamental conception of the nature of evolution.

The complex interactions of man with man in a community are usually described by such comprehensive terms as the State, the Commonwealth, or the Government. Various States differ widely in their constitution and in the degree of the complexity of their organisation, and we classify them by various general terms, such as autocracy, aristocracy, or democracy, which express somewhat loosely their leading characteristics. But, for the purpose of showing the analogy with physics, we need terms of wider import than those habitually used in politics. All forms of the State imply inter-relationship in the actions of men, and action implies movement. Thus the State may be described as a configuration or arrangement of a community of men; or we may say that it implies a definite mode of motion of man—that is to say, an organised scheme of action of man on man. Political history gives an account of the gradual changes in such configurations or modes of motion of men as have possessed the quality of persistence or of stability to resist the disintegrating influence of surrounding circumstances.

In the world of life the naturalist describes those forms which persist as species; similarly the physicist speaks of stable configurations or modes of motion of matter; and the politician speaks of States. The idea at the base of all these conceptions is that of stability, or the power of resisting disintegration. In other words, the degree of persistence or permanence of a species, of a configuration of matter, or of a State depends on the perfection of its adaptation to its surrounding conditions.

If we trace the history of a State we find the degree of its stability gradually changing, slowly rising to a maximum, and then slowly declining. When it falls to nothing a

revolution ensues, and a new form of government is established. The new mode of motion or government has at first but slight stability, but it gradually acquires strength and permanence, until in its turn the slow decay of stability leads on to a new revolution.

Such crises in political history may give rise to a condition in which the State is incapable of perpetuation by transformation. This occurs when a savage tribe nearly exterminates another tribe, and leads the few survivors into slavery; the previous form of government then becomes extinct.

The physicist, like the biologist and the historian, watches the effect of slowly varying external conditions; he sees the quality of persistence or stability gradually decaying until it vanishes, when there ensues what is called, in politics, a revolution.

These considerations lead me to express a doubt whether biologists have been correct in looking for continuous transformation of species. Judging by analogy we should rather expect to find slight continuous changes occurring during a long period of time, followed by a somewhat sudden transformation into a new species, or by rapid extinction. However this may be, when the stability of a mode of motion vanishes, the physicist either finds that it is replaced by a new persistent type of motion adapted to the changed conditions, or perhaps that no such transformation is possible, and that the mode of motion has become extinct. The evanescent type of animal life has often been preserved for us, fossilised in geological strata; the evanescent form of government is preserved in written records or in the customs of savage tribes; but the physicist has to pursue his investigations without such useful hints as to the past.

The time-scale in the transmutation of species of animals is furnished by the geological record, although it is not possible to translate that record into years. As we shall see hereafter, the time needed for a change of type in atoms or molecules may be measured by millionths of a second, while in the history of the stars continuous changes occupy millions of years. Notwithstanding this gigantic contrast in speed, yet the process involved seems to be essentially the same.

It is hardly too much to assert that, if the conditions which determine stability of motion could be accurately formulated throughout the universe, the past history of the cosmos and its future fate would be unfolded. How indefinitely far we stand removed from such a state of knowledge will become abundantly clear from the remainder of my Address.

The study of stability and instability then furnishes the problems which the physicist and biologist alike attempt to solve. The two classes of problems differ principally in the fact that the conditions of the world of life are so incomparably more intricate than those of the world of matter that the biologist is compelled to abandon the attempt to determine the absolute amount of the influence of the various causes which have affected the existence of species. His conclusions are merely qualitative and general, and he is almost universally compelled to refrain from asserting even in general terms what are the reasons which have rendered one form of animal life stable and persistent, and another unstable and evanescent.

On the other hand, the physicist, as a general rule, does not rest satisfied unless he obtains a quantitative estimate of various causes and effects on the systems of matter which he discusses. Yet there are some problems of physical evolution in which the conditions are so complex that the physicist is driven, as is the biologist, to rest satisfied with qualitative rather than quantitative conclusions. But he is not content with such crude conclusions except in the last resort, and he generally prefers to proceed by a different method.

The mathematician mentally constructs an ideal mechanical system or model, which is intended to represent in its leading features the system he wants to examine. It is often a task of the utmost difficulty to devise such a

model, and the investigator may perchance unconsciously drop out as unimportant something which is really essential to represent actuality. He next examines the conditions of his ideal system, and determines, if he can, all the possible stable and unstable configurations, together with the circumstances which will cause transitions from one to the other. Even when the working model has been successfully imagined, this latter task may often overtax the powers of the mathematician. Finally, it remains for him to apply his results to actual matter, and to form a judgment of the extent to which it is justifiable to interpret Nature by means of his results.

The remainder of my Address will be occupied by an account of various investigations which will illustrate the principles and methods which I have now explained in general terms.

The fascinating idea that matter of all kinds has a common substratum is of remote antiquity. In the Middle Ages the alchemists, inspired by this idea, conceived the possibility of transforming the baser metals into gold. The sole difficulty seemed to them the discovery of an appropriate series of chemical operations. We now know that they were always indefinitely far from the goal of their search, yet we must accord to them the honour of having been the pioneers of modern chemistry.

The object of alchemy, as stated in modern language, was to break up or dissociate the atoms of one chemical element into its component parts, and afterwards to re-unite them into atoms of gold. Although even the dissociative stage of the alchemistic problem still lies far beyond the power of the chemist, yet modern researches seem to furnish a sufficiently clear idea of the structure of atoms to enable us to see what would have to be done to effect a transformation of elements. Indeed, in the complex changes which are found to occur spontaneously in uranium, radium, and the allied metals we are probably watching a spontaneous dissociation and transmutation of elements.

Natural Selection may seem, at first sight, as remote as the poles asunder from the ideas of the alchemist, yet dissociation and transmutation depend on the instability and regained stability of the atom, and the survival of the stable atom depends on the principle of Natural Selection.

Until some ten years ago the essential diversity of the chemical elements was accepted by the chemist as an ultimate fact, and indeed the very name of atom, or that which cannot be cut, was given to what was supposed to be the final indivisible portion of matter. The chemist thus proceeded in much the same way as the biologist who, in discussing evolution, accepts the species as his working unit. Accordingly, until recently the chemist discussed working models of matter of atomic structure, and the vast edifice of modern chemistry has been built with atomic bricks.

But within the last few years the electrical researches of Lenard, Röntgen, Becquerel, the Curies, of my colleagues Larmor and Thomson, and of a host of others, have shown that the atom is not indivisible, and a flood of light has been thrown thereby on the ultimate constitution of matter. Amongst all these fertile investigators it seems to me that Thomson stands pre-eminent, because it is principally through him that we are to-day in a better position for picturing the structure of an atom than was ever the case before.

Even if I had the knowledge requisite for a complete exposition of these investigations, the limits of time would compel me to confine myself to those parts of the subject which bear on the constitution and origin of the elements.

It has been shown, then, that the atom, previously supposed to be indivisible, really consists of a large number of component parts. By various convergent lines of experiment it has been proved that the simplest of all atoms—namely, that of hydrogen—consists of about 800 separate parts; while the number of parts in the atom of the denser metals must be counted by tens of thousands.

These separate parts of the atom have been called corpuscles or electrons, and may be described as particles of negative electricity. It is paradoxical, yet true, that the physicist knows more about these ultra-atomic corpuscles, and can more easily count them than is the case with the atoms of which they form the parts.

The corpuscles, being negatively electrified, repel one another just as the hairs on a person's head mutually repel one another when combed with a vulcanite comb. The mechanism is as yet obscure whereby the mutual repulsion of the negative corpuscles is restrained from breaking up the atom, but a positive electrical charge, or something equivalent thereto, must exist in the atom, so as to prevent disruption. The existence in the atom of this community of negative corpuscles is certain, and we know further that they are moving with speeds which may in some cases be comparable to the velocity of light, namely, 200,000 miles a second. But the mechanism whereby they are held together in a group is hypothetical.

It is only just a year ago that Thomson suggested, as representing the atom, a mechanical or electrical model whose properties could be accurately examined by mathematical methods. He would be the first to admit that his model is at most merely a crude representation of actuality, yet he has been able to show that such an atom must possess mechanical and electrical properties which simulate, with what Whetham describes as "almost Satanic exactness," some of the most obscure and yet most fundamental properties of the chemical elements. "*Se non è vero, è ben trovato*," and we are surely justified in believing that we have the clue which the alchemists sought in vain.

Thomson's atom consists of a globe charged with positive electricity, inside which there are some thousand or thousands of corpuscles of negative electricity, revolving in regular orbits with great velocities. Since two electrical charges repel one another if they are of the same kind, and attract one another if they are of opposite kinds, the corpuscles mutually repel one another, but all are attracted by the globe containing them. The forces called into play by these electrical interactions are clearly very complicated, and you will not be surprised to learn that Thomson found himself compelled to limit his detailed examination of the model atom to one containing about seventy corpuscles. It is indeed a triumph of mathematical power to have determined the mechanical conditions of such a miniature planetary system as I have described.

It appears that there are definite arrangements of the orbits in which the corpuscles must revolve, if they are to be persistent or stable in their motions. For the purpose of general discussion, which is all that I shall attempt, you may take it that the number of corpuscles in such a community is fixed; and we may state that definite numbers of corpuscles are capable of association in stable communities of definite types.

An infinite number of communities are possible, possessing greater or lesser degrees of stability. Thus the corpuscles in one such community might make thousands of revolutions in their orbits before instability declared itself; such an atom might perhaps last for a long time as estimated in millionths of seconds, but it must finally break up, and the corpuscles must disperse or re-arrange themselves after the ejection of some of their number. We are thus led to conjecture that the several chemical elements represent those different kinds of communities of corpuscles which have proved by their stability to be successful in the struggle for life. If this is so, it is almost impossible to believe that the successful species have existed for all time, and we must hold that they originated under conditions about which I must forbear to follow Sir Norman Lockyer in speculating.

But if the elements were not eternal in the past, we must ask whether there is reason to believe that they will be eternal in the future. Now, although the conception of the decay of an element and its spontaneous transmutation into another element would have seemed absolutely repugnant to the chemist until recently, yet analogy with other

moving systems seems to suggest that the elements are not eternal.

At any rate it is of interest to pursue to its end the history of the model atom which has proved to be so successful in imitating the properties of matter. The laws which govern electricity in motion indicate that such an atom must be radiating or losing energy, and therefore a time must come when it will run down, as a clock does. When this time comes it will spontaneously transmute itself into an element which needs less energy than was required in the former state. Thomson conceives that an atom might be constructed after his model so that its decay should be very slow. It might, he thinks, be made to run for a million years, but it would not be eternal.

Such a conclusion is an absolute contradiction to all that was known of the elements until recently, for no symptoms of decay are perceived, and the elements existing in the solar system must already have lasted for millions of years. Nevertheless, there is good reason to believe that in radium, and in other elements possessing very complex atoms, we do actually observe that break-up and spontaneous rearrangement which constitute a transmutation of elements.

It is impossible as yet to say how science will solve this difficulty, but future discovery in this field must surely prove deeply interesting. It may well be that the train of thought which I have sketched will ultimately profoundly affect the material side of human life, however remote it may now seem from our experiences of daily life.

I have not as yet made any attempt to represent the excessive minuteness of the corpuscles, of whose existence we are now so confident; but, as an introduction to what I have to speak of next, it is necessary to do so. To obtain any adequate conception of their size we must betake ourselves to a scheme of threefold magnification. Lord Kelvin has shown that, if a drop of water were magnified to the size of the earth, the molecules of water would be of a size intermediate between that of a cricket-ball and of a marble. Now each molecule contains three atoms, two being of hydrogen and one of oxygen. The molecular system probably presents some sort of analogy with that of a triple star; the three atoms, replacing the stars, revolving about one another in some sort of dance which cannot be exactly described. I doubt whether it is possible to say how large a part of the space occupied by the whole molecule is occupied by the atoms; but perhaps the atoms bear to the molecule some such relationship as the molecule to the drop of water referred to. Finally, the corpuscles may stand to the atom in a similar scale of magnitude. Accordingly a threefold magnification would be needed to bring these ultimate parts of the atom within the range of our ordinary scales of measurement.

I have already considered what would be observed under the triply powerful microscope, and must now return to the intermediate stage of magnification, in which we consider those communities of atoms which form molecules. This is the field of research of the chemist. Although prudence would tell me that it would be wiser not to speak of a subject of which I know so little, yet I cannot refrain from saying a few words.

The community of atoms in water has been compared with a triple star, but there are others known to the chemist in which the atoms are to be counted by fifties and hundreds, so that they resemble constellations.

I conceive that here again we meet with conditions similar to those which we have supposed to exist in the atom. Communities of atoms are called chemical combinations, and we know that they possess every degree of stability. The existence of some is so precarious that the chemist in his laboratory can barely retain them for a moment; others are so stubborn that he can barely break them up. In this case dissociation and reunion into new forms of communities are in incessant and spontaneous progress throughout the world. The more persistent or more stable combinations succeed in their struggle for life, and are found in vast quantities, as in the cases of common salt and of the combinations of silicon. But no one has

ever found a mine of gun-cotton, because it has so slight a power of resistance. It, through some accidental collocation of elements, a single molecule of gun-cotton were formed, it would have but a short life.

Stability is, further, a property of relationship to surrounding conditions; it denotes adaptation to environment. Thus salt is adapted to the struggle for existence on the earth, but it cannot withstand the severer conditions which exist in the sun.

[The President here announced that he proposed to consider various theories of evolution in the heavens in the second portion of his Address, to be delivered at Johannesburg on Wednesday, August 30].

A SIMPLE METHOD OF SHOWING THE PRESENCE OF THE HELIUM FORMED FROM RADIUM BROMIDE.

By F. GIESEL.

THE detonating gas evolved from radium bromide solutions, like that expelled from crystallised aqueous radium bromide, owes its activity to traces of admixed emanation. Ramsay's discovery has proved the truth of the conjecture I have previously expressed (*Berichte*, 1902, xxxv., 3608), that we should obtain an insight into the internal processes of the radium atom if it was possible to prove the existence of a gas arising from the radium (and not from the water). The fact that only a few have succeeded in proving the presence of helium is due to the exceedingly small quantities of emanation which are formed, and to the difficulty of separating the helium in a pure state from the large quantities of detonating gas.

In order to overcome these difficulties, I put 50 m.grms. of anhydrous radium bromide into each of two Geissler tubes (1 and 2) of the ordinary form with aluminium electrodes, and exhausted as completely as possible, firstly to prevent the formation of detonating gas, and secondly to see whether the presence of water has any influence on the formation of emanation or helium. Tube 1 contained about 5 c.c., tube 2 about 15 c.c.; the first contained the salt heated to a temperature only just below its melting-point for the purpose of dehydration, and the second contained the same salt melted on a platinum wire. In tube 1, though it was heated for hours with an induction current, it was not possible to obtain such a vacuum that the luminescence of the gaseous residues in the capillary tube ceased, but was far better with tube 2. After melting off the pump the hydrogen and mercury lines were very plainly visible in tube 1 and only faintly visible in tube 2. After two months the helium line $D_3 = \lambda 587.6$ appeared in tube 1, and after six months $\lambda 502$ appeared, and also $\lambda 495$, $\lambda 470$, $\lambda 446^*$ very faintly. With tube 2, which luminesced only faintly, only the D_3 line could be perceived after this lapse of time. The lines were identified by means of a spectroscope of high dispersion by comparison with the aid of a cross-thread arrangement.

The induction current can be driven through both tubes for any length of time without affecting the helium spectrum. No change in the gas pressure of the tubes could be observed as far as can be judged by the luminescence phenomena.

It may be mentioned as a striking fact that the activity of the gas appears very small as compared with that of the detonating gas from radium solutions. The emanation thus appears to be retained firmly by the dehydrated radium bromide.

The changes of the gaseous contents of the tubes will be further examined.—*Berichte*, 1905, xxxviii., 2299.

ON THE RETROGRESSION OF SOLUBLE PHOSPHATES IN MIXED MANURES.

By GEORGE GRAY, F.C.S., Lecturer on Chemistry, Canterbury Agricultural College, Lincoln, N.Z.

THE term "retrogression" applied to superphosphate of lime implies certain chemical changes by which the soluble mono-calcic phosphate is converted into an insoluble form.

The chief advantages possessed by superphosphate over other forms of phosphatic manure lies in the fact that the phosphoric anhydride, being in a soluble form of combination, is better distributed through the soil, and brought more within the range of plant roots. In well-made superphosphate the retrogression is but small, but in cases where insufficient sulphuric acid has been employed and the raw tri-calcic phosphate is but partially decomposed, the degree of retrogression may be considerable. In the presence of undecomposed tri-calcic phosphate, mono-calcic phosphate is reduced to the condition of di-calcic phosphate. In cases where the original phosphate contains much calcic carbonate, and where a portion of this remains undecomposed, or where superphosphate is mixed with other manures containing calcic carbonate, the retrogression may proceed further, and tri-calcic phosphate may be formed. When iron is present in the raw phosphate, either as silicate or as pyrites, no action occurs; but when in the form of ferric or ferrous oxide, these form the corresponding sulphates, which react on the mono-calcic phosphate, and the retrogression is of a more serious nature. Alumina when present also causes retrogression, but the reactions are similar to those with calcium compounds. The retrograded phosphates are insoluble in water, but soluble in solutions of ammoniac citrate, and hence the term "citrate-soluble phosphates" frequently applied.

Considerable difference of opinion exists as to the agricultural value of these citrate-soluble phosphates, some agricultural chemists regarding them as being of equal value to the mono-calcic phosphate, while others consider them only of value equal to tri-calcic phosphate. Considering that the diffusive power of the phosphoric acid present has been destroyed, my own practice has been to value them only as tri-calcic phosphate. Manufacturers generally argue that, as the tri-calcic phosphate has been rendered once soluble at their expense, they should receive credit for it, while agriculturists maintain that it is only fair that they should pay a higher price for the phosphoric acid actually existing in the soluble form, and that the retrograde phosphate should be assessed at a lower value.

In the blending of manures, such as is largely done by our freezing companies, mistakes are often made, and the value of the superphosphate used considerably reduced by retrogression. Farmers, again, by mixing superphosphate with other substances in order to improve the mechanical texture, and to cause the manure to pass more easily through the drill, often completely destroy the soluble phosphate for which they have paid an increased price, the comparative market value of the soluble to the insoluble phosphate being about 100—63.

The object of the present investigation was to ascertain the nature of the retrogression, and the rate at which it proceeds in mixtures of superphosphate and other manures such as have come under notice as having been used in actual practice. In the experiments a good, well-made superphosphate was employed, containing "soluble" phosphate equal to 17.74 per cent of phosphoric anhydride. This was mixed with equal parts of other manures and the amounts of water-soluble, citrate-soluble, and insoluble phosphate determined from time to time. Briefly, the method of analysis consisted in extracting the mixtures with pure water, and afterwards with a neutral solution of ammonium citrate, determining the total phosphoric anhydride, that soluble in water, and that insoluble in ammonium citrate, the citrate soluble being taken by

* Himstedt and G. Meyer (*Berichte d. Naturf. Ges.*, at Freiburg, i. B., xvi., 10, May, 1905) have recently arrived at the same results by using dehydrated radium bromide in an electrodeless quartz tube with Tesla currents.

TABLE I.—Showing Retrogression of Soluble Phosphoric Anhydride in Mixed Manures.

	Original mixture.	Three hours.	Twenty four hours.	Six days.	Twelve days.	Eighteen days.
1. A Mixture of equal parts of Superphosphate and Bone-dust :—						
Phosphoric anhydride—Soluble in water.. ..	8·87	8·87	8·87	8·87	8·62	8·62
Citrate-soluble	1·57	3·45	3·95	3·70	3·95	3·95
Insoluble	9·63	7·75	7·25	7·50	7·50	7·50
Total	20·07	20·07	20·07	20·07	20·07	20·07
2. Equal parts of Superphosphate and Coral Queen Guano :—						
Phosphoric anhydride—Soluble in water.. ..	8·87	8·87	8·57	8·37	8·37	8·25
Citrate-soluble	3·43	10·89	7·94	9·64	8·64	8·26
Insoluble	12·96	5·50	8·75	7·25	8·25	8·75
Total	25·26	25·26	25·26	25·26	25·26	25·26
3. Equal parts of Superphosphate and Chesterfield Guano :—						
Phosphoric anhydride—Soluble in water.. ..	8·87	7·87	7·37	4·87	4·00	3·37
Citrate-soluble	2·24	1·95	1·45	3·70	3·32	4·70
Insoluble	8·21	9·50	10·50	10·75	12·00	11·25
Total	19·32	19·32	19·32	19·32	19·32	19·32
4. Equal parts of Superphosphate and Basic Slag :—						
Phosphoric anhydride—Soluble in water.. ..	9·43	4·00	2·12	1·37	1·25	1·12
Citrate-soluble	2·49	15·67	16·05	14·80	15·92	14·80
Insoluble	10·25	2·50	4·00	6·00	5·00	6·25
Total	22·17	22·17	22·17	22·17	22·17	22·17
5. Equal parts of Superphosphate and Kainit :—						
Phosphoric anhydride—Soluble in water.. ..	8·87	8·87	8·87	8·50	8·25	8·25
Citrate-soluble	0·72	1·75	1·75	0·62	1·62	2·37
Insoluble	1·03	0·00	0·00	1·50	0·75	0·00
Total	10·62	10·62	10·62	10·62	10·62	10·62
6. Equal parts of Superphosphate and Slaked Lime :—						
Phosphoric anhydride—Soluble in water.. ..	8·87	0·50	0·00	0·00	0·00	0·00
Citrate-soluble	0·72	7·37	10·62	6·87	7·87	6·62
Insoluble	1·03	2·75	0·00	3·74	2·75	4·00
Total	10·62	10·62	10·62	10·62	10·62	10·62
7. Equal parts of Superphosphate and Ground Lime-stone :—						
Phosphoric anhydride—Soluble in water.. ..	8·87	7·87	1·75	1·12	0·75	1·25
Citrate-soluble	0·72	2·03	8·15	8·78	9·15	8·65
Insoluble	1·06	0·75	0·75	0·75	0·75	0·75
Total	10·65	10·65	10·65	10·65	10·65	10·65

TABLE II.—Showing Percentage of Total Soluble Phosphoric Anhydride Reduced.

Mixture.	Three hours.	Twenty-four hours.	Six days.	Twelve days.	Eighteen days.
1. Superphosphate and bone-dust ..	0·0	0·0	0·0	2·8	2·8
2. Superphosphate and Coral Queen guano	0·0	3·3	5·3	5·3	7·0
3. Superphosphate and Chesterfield guano	11·2	16·9	44·8	54·9	62·0
4. Superphosphate and basic slag ..	57·6	77·5	85·4	86·7	88·1
5. Superphosphate and kainit	0·0	0·0	4·1	6·9	6·9
6. Superphosphate and slaked lime ..	94·3	100·0	100·0	100·0	100·0
7. Superphosphate and crushed lime-stone	11·2	80·2	87·3	91·5	85·9

difference. The method of determining citrate-soluble phosphoric anhydride is not by any means a satisfactory one, but still it is the best in use. Ammonic citrate solution, even when neutral, attacks the various forms of phosphates in different degrees. Thus the manures used in the present case were found to yield to neutral ammonic citrate solution proportions of tri-calcic phosphate equivalent to phosphoric anhydride as follows:—

Bone-dust, 9 per cent of total phosphoric anhydride; Chesterfield guano, 17.5 per cent; Coral Queen guano, 18.5 per cent; basic slag, 16.4 per cent.

Table I. shows the condition of the phosphoric anhydride on first mixing the manures, and at intervals afterwards. The results are all expressed as phosphoric anhydride.

Table II. shows the percentage of the total phosphoric anhydride present that has retrograded during different periods.

Superphosphate and Bone-dust.—In this mixture the amount of retrogression is small, and proceeds but slowly. The citrate-soluble phosphoric anhydride is increased at the expense of the insoluble phosphate. This is probably due to the solvent action of ammonium citrate on tri-calcic phosphate before mentioned. The low degree of retrogression in the case of the bone-dust mixture may to some extent be due to the protection of the tri-calcic phosphate afforded by the ossein present. Doubtless bone-dust is the best form in which to use tri-calcic phosphate for mixing with superphosphate.

Superphosphate and Coral Queen Guano.—The sample of Coral Queen guano used contained 63.9 per cent of tri-calcic phosphate and 1.1 per cent of calcic carbonate, together with about 8.8 per cent of iron oxide. Like bone-dust, this manure appears to be slow in its action, only 7 per cent of the soluble phosphoric anhydride being reduced after eighteen days. The amount of citrate-soluble phosphate is considerably above that, due to retrogression, as in the case of bone dust, and the proportion is higher than that in the latter, due to the greater solvent action of the citrate solution on the guano.

Superphosphate and Chesterfield Guano.—This guano is characteristic in containing a high percentage of calcic carbonate (37.9 per cent), and, as may be expected, retrogression is considerable, and has proceeded not only to the stage di-calcic phosphate, but beyond this, to form insoluble tri-calcic phosphate.

Superphosphate and Basic Slag.—The influence of basic slag on superphosphate is due to two causes—the action of calcic oxide and the action of proto- and per-salts of iron. As is shown later, calcic oxide is very active in retrogression, and the oxides of iron produce reduction of the worst kind. Table II. shows that within three hours over 50 per cent of the acid was in an insoluble form. The production of phosphates of iron has increased the proportion of citrate-soluble compound considerably.

Superphosphate and Kainit.—The action of kainit is due mainly to the salts of magnesium present. The retrogression is small, only about 7 per cent of the acid being reduced in eighteen days.

Superphosphate and Slaked Lime.—The retrogression of superphosphate with slaked lime is particularly rapid, 94 per cent of the soluble phosphoric anhydride being reduced within three hours, and the whole amount present within twenty-four hours. When mixed considerable heat is evolved, and moisture evaporated. It is mainly the di-calcic phosphate that is formed at first, although probably with longer time this would further revert to the form of tri-calcic phosphate.

Superphosphate and Ground Limestone.—The effect of calcium carbonate, although not so great as that of slaked lime, is yet considerable. When mixed with superphosphate carbon dioxide is at once evolved, and within twenty-four hours 80 per cent of the phosphoric anhydride present is converted into a form in which it is soluble in ammoniac citrate.—*Transactions of the Australasian Association for the Advancement of Science*, 1904, p. 157.

Gentiopirine.—Georges Tanret.—Gentiopirine is a crystalline glucoside, hitherto almost unknown, which was discovered by Kromayer in the fresh root of gentian. It has since been prepared by a long and difficult series of manipulations. The author now discovers a simpler and more practical method for its preparation. After preparing it in a pure state, he investigates its properties and composition.—*Comptes Rendus*, cxli., No. 3.

NOTICES OF BOOKS

Spectroscopy. By E. C. C. BALY, F.I.C. London, New York, and Bombay: Longmans, Green, and Co. 1905.

The appearance at last of a really satisfactory text-book of spectroscopy will be heartily welcomed by the many who have had occasion to lament the non-existence of a book suited both for the use of the student as a text-book to be worked through, and also as a work of reference to be consulted on special points. For both purposes this book will be found excellent. The students who use it will derive the greater benefit from it because it is the work of a teacher who understands the difficulties and stumbling blocks which the most intelligent are bound to meet with, and while the treatment is by no means elementary the clearness of the author's style makes the book quite suitable for being put into the hands of those who have no previous acquaintance with the subject. Great attention is paid to the detailed description of the construction and manipulation of various instruments, the subject being presented specially from the practical point of view, but no branch is neglected, and the chapters on the more theoretical aspects form some of the most interesting parts of the book. The omission of set tables of wave-lengths enables the author to include much interesting and important matter which must otherwise have been sacrificed, and is hence quite justified. The book is fully and carefully illustrated throughout, and contains very complete diagrams and cuts of Rowland's grating ruling engines.

A Systematic Course of Practical Organic Chemistry. By LIONEL GUY RADCLIFFE, F.C.S., and FRANK STURDY SINNATT, F.C.S. London, New York, and Bombay: Longmans, Green, and Co. 1905.

ALTHOUGH this book possesses many valuable features, on the whole it cannot but be regarded as disappointing, and in spite of the fact that it can be recommended in default of a better, we consider that the ideal book on practical organic chemistry is yet to be written. The chief respects in which the book falls short are, firstly, the lack of such systematic arrangement as would enable the student to realise that organic chemistry is not merely a chaotic accumulation of unrelated facts, and secondly the failure to develop the originality of the student to the utmost extent, so that the book hardly seems likely to stimulate the spirit of research latent in the mind of the average young chemist. This latter defect is most noticeable in the special work for advanced students, which should have provided scope for the display of a little more enterprise on the part of the worker than is necessary for a few additional preparations and qualitative reactions. Apart from these shortcomings, which it possesses in common with so many of its rivals, the book has numerous good points. The directions for the experiments appear to be adequate without being redundant, and the repeated instructions to "weigh the yield," thus keeping the quantitative aspect of the reactions constantly before the worker, are an excellent feature. All illustrations are omitted, the authors believing that it is best to have set up in the laboratory a model of the apparatus to be used, or else to allow the students to submit sketches of what they consider suitable arrangements for the various experiments.

Report on the Manufacture of Paints and Colours containing Lead. By T. M. LEGGE, M.D., H.M. Medical Inspector of Factories. London: Darling and Son, Ltd. 1905.

In this report of H.M. Medical Inspector of Factories the incidence of plumbism in paint and colour works is discussed, the statistics collected showing that most of the poisoning which occurs in such works is undoubtedly due

to the dust formed during the process of mixing and grinding white-lead. In view of the fact that at present very little is done to remove or even diminish this source of danger, the Inspector's recommendations regarding the regulations which should be enforced will be read with great interest; these suggested regulations are far less stringent than those which the German Federal Council decreed in 1903, and of which a translation is appended. The report is illustrated by photographs of paint-grinding machines and by diagrams showing various fan arrangements for removing white-lead dust in paint works.

Le Four Electrique, Son Origine, Ses Transformations, et Ses Applications. ("The Electric Furnace, its Origin, Transformations, and Applications"). By ADOLPHE MINET. (Part I.). Paris: A. Hermann. 1905.

THE increasing application of the electric furnace in many industrial processes has led to the production of important additions to the literature of the subject, of which additions this bids fair to be one of the most valuable. The author divides the history of the electric furnace into three periods; the first, from 1808 to 1886, he describes as the laboratory period, at the beginning of which the voltaic arc was discovered by Davy. Although towards the end of this period Borchers had invented a resistance furnace by means of which he had succeeded in reducing some refractory oxides, and Louis Clerc with an arc furnace had fused most of these oxides, the electric furnace in general had as yet found no applications outside the laboratory. The second period in the history lasts from 1886 to 1890, and sees the beginning of industrial applications which during the last period (1890 to the present day) have developed to such a striking extent. The present volume includes, first, a plan of the whole work, in which the parts played by the various investigators are briefly outlined. In this connection it is curious to notice that in the third period, in which we should have expected to find Moissan's name pre-eminent, it is only mentioned quite incidentally, though the value of Bullier's work is recognised. The rest of this part contains an account of the first period, which the author considers both from the descriptive and theoretical points of view; in the last chapters devoted to the theory, physical units, electrical systems and cycles, and the fundamental laws of electro-chemistry are discussed, and tables of various important constants are given. Although the subject, as far as this period is concerned, may be regarded as of little more than theoretical interest, the author has laid in this part the foundations of a most useful treatise, if the succeeding four volumes fulfil the promise of the first.

Les Nouveautés Chimiques pour 1905. ("Chemical Novelties for 1905"). By CAMILLE POULENC, Docteur ès Sciences. Paris: J. B. Baillière et Fils. 1905.

In this volume the author has followed the general plan adopted in the preparation of preceding volumes. It contains descriptions of the recent improvements and modifications which have been suggested with regard to various kinds of apparatus used in chemical work, dealing first with the general applications of physics to chemistry, which includes the discussion with illustrations of new apparatus for determining the physical properties of substances. The next section is devoted to more purely chemical operations, such as distillation, filtration, &c.; a good deal of space being somewhat unadvisedly given to the description of Verneuil's apparatus for the artificial production of rubies by fusion. The chapter on electro-chemistry includes all the apparatus employed by the Curies in the study of radio-activity, as well as Commelin and Vial's mixed accumulator. In the pages on analytical processes many useful novelties collected from all sources are described, and the analyst will be likely to glean many hints from it.

CORRESPONDENCE.

ZINC DUST.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS of August 4th (vol. xcii., p. 56) appears a paper by A. B. Stevens on the above subject, which kindly allow me to supplement with a few observations of my own.

From Mr. Stevens' paper it might be inferred that zinc dust is of special manufacture; but, as is well known, it is a by-product, and although at the present moment it is in fair demand and the price comparable with that of reguline zinc, it is not manufactured designedly.

It generally appears in commerce packed in old petroleum casks, from which it abstracts relatively large amounts of petroleum of a particularly disgusting odour; this is probably the source of the oil recovered by Mr. Stevens, and it is not, as the paper might suggest, a condensation product from the manufacture of the dust itself.

Quite recently I had to heat half a ton of zinc dust to 600° F. in a closed vessel, and the escaping gas and vapour had such an overpowering smell that I had to suspend operations until provision could be made to deal with it.

I have also remarked the evolution of ammonia on heating with caustic alkali, and on this account have discontinued the use of zinc dust in Kjeldahl operations, but since I failed to obtain ammonia when using caustic soda from metallic sodium, I ascribed it to the reduction of the ever-present nitrates in the commercial alkali.

I would also point out that almost everything in a laboratory becomes contaminated with ammonia unless well protected from the atmosphere, and that many finely-divided solids, such as zinc dust, have a special faculty for condensing vapours and gases, possibly acting like charcoal in this respect. It is almost inconceivable that a metallic body such as zinc dust should be able to fix atmospheric nitrogen; but when one considers that the normal atmosphere contains traces of ammonia, it is not surprising that the dust should absorb it on exposure to the air.

It is perhaps not generally known that zinc dust is sometimes pyrophoric, and if suspended in the air something like an explosion may occur if it becomes ignited. I have seen a 5-cwt. cask smoulder until it was converted into oxide to a depth of 4 or 5 inches, after which apparently it smothered itself out.

Under the microscope zinc dust is seen to consist of metallic globules 1 to 5 micromillimetres in diameter mixed with some oxide and impurities; if this oxide be removed by acid, washing, &c., the dust can be smelted down to reguline metal if the air be excluded. Ordinary zinc dust cannot be so fused, but, under certain conditions, can be smelted into a curious crystalline mass, easily pulverable, and very brittle.—I am, &c.,

WILLIAM RAMSAY.

Birkenhead Iron Works, August 9, 1905.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 3, July 17, 1905.

Preparation of Binary Compounds of the Metals by means of Aluminium.—C. Matignon and R. Trannoy.—The authors prepare a number of phosphides, arsenides, silicides, and borides by application of the reducing properties of finely-divided aluminium.

Reduction of Thorium Oxide by means of Amorphous Boron, and Preparation of two Thorium Borides.—M. Binet du Jassonneix.—If an intimate mix-

ture of thorium and boron is heated in a charcoal crucible in the electric furnace, at a pressure of 100 volts and with current of 500 amperes, at the end of three minutes the mixture does not melt. It only melts when the current is increased to 700 amperes. Thorium bromides, shown by analysis to have the composition ThBr_6 and ThBr_4 , can then be separated from the melt.

Certain Reactions of Gaiac Resin.—P. Petit and M. Mayer.—The authors investigate the colour reaction given by gaiac resin, and find that tincture of gaiac gives a very strong blue colouration in presence of iron or manganese salts.

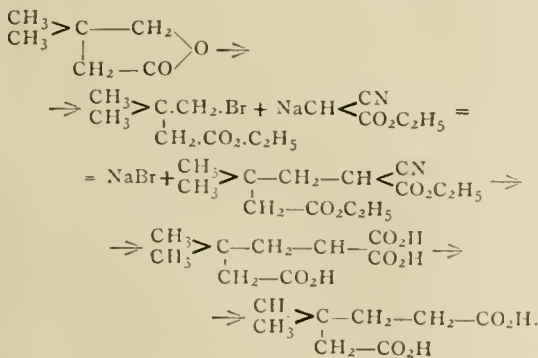
Action of Chloroacetic Ethers on the Halogen-magnesium Derivatives of Orthotoluidine.—F. Bodroux.—Ethyl monochloroacetate reacts energetically on magnesium orthotoluidine iodide. The author examines two special cases. 1. When the organo-magnesium salt is in ether solution, the orthoiodoacetoluide is formed almost quantitatively, $\text{CH}_3\text{—C}_6\text{H}_4\text{—NH—CO—CH}_2\text{I}$. 2. When, as sometimes happens, the organo-magnesium salt coagulates spontaneously, the yield of iodoacetoluide is small; the principal product of the operation in this case being ethyl iodacetate.

Action of Ethylamine and Isobutylamine on Cæsium.—E. Rengade.—The author's experiments show that the primary amines of the fatty series react on cæsium, giving as a final product a substituted amide; in the case of the first members of the series, an unstable ammonium compound is formed transitorily. Such derivatives are unstable; they decompose very easily when in contact with air at a temperature of about 110° . With water they give a cæsium hydrate, and the amine is formed again. The author also finds that it is very easy to pass from one of these amides to the others by the direct action of the corresponding amines or ammonia. Thus, liquefied ammonia dissolves cæsium ethylamide, but, after evaporation of excess of the liquid, crystals of cæsium amide remain. The loss of weight of the tube exactly corresponds to the substitution of CH_3 by H , $\text{CH}_3\text{NHCs} + \text{NH}_3 = \text{CH}_3\text{NH}_2 + \text{NH}_2\text{Cs}$.

Attempted Reduction in the Series of Dinitrodiphenylmethane Compounds.—H. Duval.—The author's experiments were made on dipara-aminodiphenylmethane purified by distillation *in vacuo*.

Condensation of Chloral with the Aromatic Hydrocarbons under the Influence of Aluminium Chloride.—Adolphe Dinesmann.—The author investigates the reaction of chloral on benzene, and finds that excellent yields are obtained under his experimental conditions, trichloromethylphenylcarbinol, $\text{C}_6\text{H}_5\text{—CHOH—CCl}_3$, being formed, resulting from the integral union of equal molecules of benzene and chloral. By repeating the reaction with toluene, paraxylene, and anisol, he shows the reaction to be of a general nature.

3,3-Dimethylbutyrolactone.—G. Blanc.—The author obtains the β -dimethyladipic acid, starting from M. Blaise's lactone, by the following series of transformations:—



Action of Tetrabromide of Acetylene and of Aluminium Chloride on Toluene.—James Lavaux.—The author investigates the theory of the reaction of a mixture of acetylene tetrabromide and aluminium chloride on toluene.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxviii., No. 8, 1905.

Higher Oxidation Products of Chromium.—E. H. Riesenfeld, H. E. Wohlers, and W. A. Kutsch.—Wieder has already prepared (blue) salts of the acid H_3CrO_7 . The author has now succeeded in obtaining the ammonium, sodium, and potassium salts of the higher acid, H_3CrO_8 , by cooling a mixture of water, 25 per cent alkali, and 50 per cent chromic acid anhydride solution, and adding, drop by drop, a 30 per cent solution of hydrogen peroxide. The temperature must not be allowed to exceed 0° . The solution darkens, and the red salt crystallises on the bottom of the vessel; the yield corresponds to about 50 per cent of the hydrogen peroxide used. The blue lower salts, e.g., $(\text{NH}_4)_2\text{H}_2\text{CrO}_7$, are obtained similarly, but the chloride of the metal and hydrochloric acid are used instead of caustic alkali. The red salts, e.g., $(\text{NH}_4)_3\text{CrO}_8$, are very unstable, and readily give up oxygen, forming an amorphous powder. They are insoluble in pure alcohol and ether, but are decomposed, yielding chromate and aldehyde if more than 50 per cent of water is present in the alcohol. All three salts are slightly soluble in cold water. On warming in neutral and alkaline solutions, chromate is formed, while in strongly acid solution perchromic acid is produced, and is almost immediately for the most part converted into chromic salt. On heating the salts oxygen is slowly given up by the potassium salt at 170° , the sodium salt at 110° , and the ammonium salt at 40° ; when these temperatures are slightly exceeded, explosive decomposition takes place, and chromic oxide is formed. With concentrated sulphuric acid a violent reaction takes place, and chromous oxide is formed in green flakes. In the case of the ammonium salt, a blow will cause a sharp detonation.

Metallic Calcium.—K. Arndt.—The author has had occasion to examine alloys of calcium and aluminium containing 25, 50, and 80 per cent calcium (denoted hereafter by M_{25} , M_{50} , and M_{80} respectively). Of these, the last is by far the least brittle. The melting-points are M_{25} 765° , M_{50} 1050° , and M_{80} 600° . Although silicon was also present in the alloys from M_{80} , pure calcium could be distilled off at a red heat *in vacuo*, neither silicon nor aluminium coming over. When M_{50} was distilled from an iron tube the calcium coming over contained both aluminium and iron, but was quite pure when a porcelain crucible was used. Thus even large amounts of aluminium can be separated from calcium by simple distillation in a high vacuum. It is noticeable that the melting-point of M_{50} is 250° higher than that of the component (Ca 800°) of higher melting-point. Calcium-aluminium alloys may be prepared by introducing calcium into aluminium, which is fused under potassium chloride. Considerable heat is evolved, and some of the calcium burns away. They may also be prepared by electrolysis, using as cathode melted aluminium. By using an alloy of aluminium and copper as cathode, the author obtained an alloy containing aluminium, copper, calcium, and traces of silicon on electrolysing fused calcium chloride. He also succeeded in obtaining electrolytically alloys of aluminium and barium containing up to 45 per cent of barium.

Explosive Mercury Salts.—K. A. Hofmann.—The author is of the opinion that except in the case of such endothermic substances as cyanic acid and acetylene, the entrance of mercury into the molecule does not influence the energy content of the system sufficiently to render explosive decomposition possible. Chlorato-mercuric aldehyde, $\text{C}_2\text{Hg}_2\text{ClO}_4\text{H}$, is prepared by dissolving mercuric oxide in aqueous chloric acid, adding alcoholic aldehyde, and allowing to crystallise in the cold. The crystals

explode so violently that they can only be touched very cautiously with a soft brush without suffering decomposition. It is not possible to perform a combustion for the determination of carbon, for on mixing with copper oxide the crystals explode, but from other analytical data and from their behaviour the formula is undoubtedly $C_2Hg_2ClO_4H$. Chlorato-mercuric aldehyde is prepared by adding pure acetylene to an aqueous mercuric chlorate solution. It is explosive, but far less so than the dimercure compound. If these chlorates are compared with the corresponding similarly constituted nitro-mercury aldehydes, $NO_3Hg(Hg):C\cdot COH$ and $NO_3Hg(Hg_2O):C\cdot COH$, as regards their explosiveness, the difference in energy between chloric and nitric acids is very striking. Both nitrates can be ignited without danger, merely a slight detonation occurring, which does not injure even a thin glass vessel. Comparing the heat of formation (in water) of $HNO_3 = +48.8$ cal. and $HClO_4 = 23.9$ cal. it must be deduced that, apart from the thermic effect of the formation of calomel from the chlorates, these give up 24.9 cal. more energy than the nitrates, which explains the strikingly different activity. If acetylene is led into an aqueous mercury perchlorate solution, the white powder which separates is somewhat less sensitive to friction than the chlorate, but decomposes with about the same violence when it comes in contact with a flame. By the action of acetylene upon a mixture of mercuric nitrate solution with excess of potassium nitrite in ice-cold water containing 1 per cent of free nitric acid, a compound, $NO_2Hg(Hg):C\cdot COH$, is formed. Friction and also gentle heating cause this to decompose violently with an explosion.

No. 9, 1905.

Sulphonic Acid Anhydrides.—O. C. Billeter.—By heating benzene sulphonic chloride with silver cyanate to 140° and extracting the product with ether, large clear crystals of benzene sulphonic acid anhydride are obtained. These melt at 92° , and are soluble in chloroform, benzene, and warm ether; they deliquesce in air, forming benzene sulphonic acid, but remain unchanged in cold water for a long time, dissolving on warming. By examining quantitatively their behaviour towards water and alcohol, the author has conclusively proved that these crystals are the true anhydride, the product described by Abrahall being a decomposition product of the anhydride, *i.e.*, the free acid. By the action of methyl sulphonic chloride on silver cyanate a substance is obtained which resembles the synthetic anhydride very closely in properties, and, like benzene sulphonic acid anhydride, gives the ethyl ester when treated with impure ether. The anhydride prepared by the action of methyl sulpho-chloride on silver methyl sulphate melts at 71° , deliquesces in the air, and is decomposed by alcohol and hot water rapidly and by cold water slowly.

Action of Sodium Polysulphide on Sodium Hydro-sulphite.—A. Binz.—Sodium hydrosulphite does not react with sodium sulphide, but a vigorous reaction takes place with sodium polysulphide, H_2S and S being formed and the solution being decolourised. In presence of caustic soda definite reactions take place, and the sodium hydrosulphite takes up sulphur from the polysulphide into the sulphonyl-complex. From quantitative experiments in which the sulphur which can be precipitated by cadmium carbonate is determined before and after the reaction, it appears that the polysulphide sulphur which enters the hydrosulphite again appears as simple sodium sulphide; hence it seems probable that a thiosulphite, $NaS\cdot SO_2Na$, is formed during the reaction, and again decomposes, forming mono-sulphide and sulphite. The action of thiosulphate upon hydrosulphite is similar to that of polysulphide, but slower. If sodium hydrosulphite and thiosulphate are allowed to stand in alkaline solution for several hours, sodium sulphide is formed. This seems to explain the appearance of sodium sulphide in originally perfectly pure alkaline hydrosulphite solutions which are not freshly made; thiosulphate

forms in them $2Na_2S_2O_4 = Na_2S_2O_3 + Na_2S_2O_5$, and then reacts as above.

Double Salts of Palladium Chloride and Bromide.—A. Gutbier.—Like platinum chloride, palladium chloride and bromide form double compounds with the halogen derivatives of organic bases. The author has prepared these double compounds with aniline and toluidine chlor- and brom-hydrate, and has found that the products result only when a small quantity of the chlor- or brom-hydrate of the organic base, dissolved in water, is allowed to act upon excess of the solution of palladium haloid. If this action is reversed, *i.e.*, if small quantities of the palladium haloid solution are allowed to act upon excess of the aqueous solution of the organic compound, no double salts are obtained, but compounds which are derivatives of palladosamine chloride or bromide. The same products are obtained by the action of the free bases upon the palladium haloid; it appeared to be immaterial whether the base was mixed directly with the solution of palladium haloid, or whether it was employed in alcoholic solution. The author has established the identity of these products as derivatives of palladosamine, $Pd(NH_3)_2OH$; they are characterised by dissolving in ammonia, forming colourless solutions, which after boiling are precipitated by the corresponding haloid acid, giving the palladosamine chloride or bromide.

Quantitative Separation of Gold from other Metals by Hydrazine and Hydroxylamine Salts.—P. Jannasch and O. von Mayer.—Gold is precipitated quantitatively in neutral, acid, or alkaline solution by means of hydrazine. According to the temperature and the presence of certain other elements, the gold precipitate differs in character and colour, *e.g.*, it is powdery in presence of chromium, forms spongy conglomerates in zinc solutions, &c., though not the slightest trace of the foreign metal is associated with the gold. Hydroxylamine also separates gold quantitatively in hydrochloric acid solution, but not so energetically as hydrazine, and not at a temperature below 80° . By means of hydrazine chlorhydrate gold can be separated from most metals, tin being the most notable exception; the gold precipitates always contain more or less tin.

Processes in the Reduction of Iron.—Rudolf Schenck and W. Heller.—When carbon monoxide acts at approximately atmospheric pressure on nickel and cobalt, and the changes of pressure at constant volume are observed, the reaction ceases at about half the initial pressure, *i.e.*, when equilibrium has ensued between the two gases carbon monoxide and solid carbon. In presence of iron the case is different, the pressure at which the reaction comes to a standstill being very small. This can only occur if the metal does not act purely catalytically, but itself takes part in the reaction. Pure carbon monoxide cannot oxidise iron. Hence the authors concluded that the action consists of two processes. Firstly, the metal acts purely catalytically, causing the monoxide to be split up into dioxide and carbon until the quantity of the dioxide is increased, so that the two oxides are no longer in equilibrium with the metallic iron; then the metal is oxidised according to the equation $Fe + CO_2 = FeO + CO$, the CO being again decomposed into C and CO_2 . These two processes finally cease when perfect equilibrium has resulted between iron, iron oxide, carbon, and the two oxides. On examining the conditions for the equilibria between carbon and the two oxides, and also between iron, ferrous oxide, carbon monoxide, and carbon dioxide, it is found that a perfectly definite partial pressure and a perfectly definite total pressure of the two oxides of carbon correspond to every temperature. The knowledge of the pressure of total equilibrium is of importance in the blast-furnace process. Ferrous oxide is reduced by carbon monoxide in the presence of carbon only if the total pressure of carbon monoxide and di-oxide is less than the pressure of total equilibrium. If the pressure of the gaseous mixture is greater at the same temperature, re-oxidation of the metallic iron and separation of carbon result, which is what occurs oc-

casionaly in the furnace. The authors have determined the pressures of total equilibrium for a large number of temperatures between 400° and 800° by two different methods, obtaining perfectly concordant results, and have also studied the behaviour of metallic manganese towards carbon monoxide. Manganese being much more easily oxidised than iron, it was to be expected that the pressure of total equilibrium would be much less for manganese than for pure iron. This was completely confirmed by experiment, and it was found impossible to measure the pressures at temperatures below 1200°. On the large scale, when the carbon monoxide is prepared from the air, in consequence of the presence of nitrogen the sum of the partial pressures of CO and CO₂ must not exceed one-third of an atmosphere = 250 m.m. Hence the reduction of ferrous oxide occurs at all temperatures at which the equilibrium pressure is greater than 250 m.m.; i.e., at all temperatures above 695°. If manganese is present in the iron the limit of reduction lies much higher than 695°.

Relations of the Different Modifications of Carbon to one another.—Rudolf Schenck and W. Heller.—Since at high temperatures both amorphous carbon and the diamond pass into graphite, the last is regarded as the most stable of the carbon modifications. The different modifications undoubtedly possess different amounts of free energy, and hence the constants of equilibrium between CO, CO₂, and the different forms of solid carbon must possess different values at the same temperature, being greatest for the most labile form and least for the most stable. If the total pressure of the two gases is denoted by P, the equilibrium constant of the carbon equilibrium (C, CO, CO₂) by ζ, and that of the system Fe, FeO, CO, CO₂ by η; then $P = \zeta \cdot \frac{1 + \eta}{\eta}$, whence

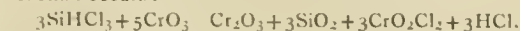
the values of ζ for the different carbon modifications are directly proportional to the pressures of total equilibrium (at constant temperature). The authors determined the values of ζ for the different modifications for temperatures ranging from 400—800°, and on representing these graphically they found that the temperature-pressure curves differed considerably. Amorphous sugar carbon showed the highest pressure, and is the most labile form, while graphite is the most stable. Comparing the carbon prepared from carbon monoxide with graphite they obtained the same curve, whence they concluded that this carbon is merely very finely divided graphite. The curve for the diamond is intermediate between that for graphite and amorphous carbon, being nearer the latter. The diamond is thus a meta stable form of carbon.

Determination of Sugar with Fehling Solution.—F. P. Lavallo.—Already noticed.

Colloid Copper Oxide.—H. Ley.—For preparing colloid oxide of copper a salt has to be used which contains a very feeble acid constituent. Copper succinimide is well suited for this purpose. This salt is prepared by the action of a copper-mercury amalgam on mercury succinimide. The aqueous solution of this salt, on being allowed to stand for some days, gradually changes in colour from blue-green to brown. On the addition of electrolytes, such as the chlorides and nitrates of potassium and barium, a brown flocculent copper oxide appears, which may be separated from the unchanged succinimide by dialysis. Hence the brown solution contains the copper oxide in the colloid condition. Like most other metallic hydroxide colloids, it is positive, and migrates to the cathode.

Silico-chloroform.—Otto Ruff and Kurt Albert.—The authors could not succeed in discovering any new method of preparing silico-chloroform, but they have investigated the properties of the compound, using a purified specimen prepared in the usual way. The boiling-point they found to be 33° and melting-point -134° absolute; the density at 15° = 1.3438. When led through a heated glass tube the compound is decomposed according to the equation $4\text{SiHCl}_3 \rightleftharpoons \text{Si} + 3\text{SiCl}_4 + 2\text{H}_2$, which is reversible at 800°.

Silico-chloroform does not react with metals, aluminium chloride, sulphur, and red phosphorus. It possesses the power of reducing oxides, e.g., with CrO₃ the following reaction occurs:—



With sulphur trioxide the following equation apparently represents the action which occurs:—



Arsenious and antimonious oxides are both reduced to the metal when SiHCl₃ acts upon them in alkaline solution. With ammonia the following action takes place:— $\text{SiHCl}_3 + 4\text{NH}_3 = \text{SiNH}_3 + 3\text{NH}_4\text{Cl}$. The silicon nitrogen hydride is very readily decomposed, and hence its investigation presents many difficulties, but the authors have succeeded in proving that it is a derivative of tetravalent silicon; apparently the tetravalent silicon in silico-chloroform and its derivatives never passes into trivalent silicon, splitting off H, and forming silicon hexachloride, for instance.

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THE CHEMICAL NEWS.

VOL. XCII., No. 2387.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION. SOUTH AFRICA, 1905.

By G. T. BEILBY, President of the Section.

IN scanning the list of the elements with which we are thoughtfully supplied every year by the International Committee on Atomic Weights, the direction in which our thoughts are led will depend on the particular aspect of chemical study which happens to interest us at the time. Putting from our minds on the present occasion the attractive speculations on atomic constitution and disintegration with which we have all become at least superficially familiar during the past few years, let us try to scan this list from the point of view of the "plain man" rather than from that of the expert chemist. Even a rudimentary knowledge will be sufficient to enable our "plain man" to divide the elements broadly into two groups—the actually useful and the doubtfully useful or useless. Without going into detail we may take it that about two-thirds would be admitted into the first group, and one-third into the second. It must, I think, be regarded as a very remarkable fact that of the eighty elements which have had the intrinsic stability to enable them to survive the prodigious forces which must have been concerned in the evolution of the physical universe, so large a proportion are endowed with characteristic properties which could ill have been spared either from the laboratories of Nature or from those of the Arts and Sciences. Even if one-third of the elements are to be regarded as waste products or failures, there is here no counterpart to the reckless prodigality of Nature in the processes of organic evolution.

If we exclude those elements which participate directly and indirectly in the structure and functions of the organic world, there are two elements which stand out conspicuously because of the supreme influence they have exercised over the trend of human effort and ambition. I refer, of course, to the metals gold and iron.

From the early beginnings of civilisation gold has been highly prized and eagerly sought after. Human life has been freely sacrificed in its acquirement from natural sources, as well as in its forcible seizure from those who already possessed it. The "Age of Gold" was not necessarily "The Golden Age," for the noble metal in its unique and barbaric splendour has symbolised much that has been unworthy in national and individual aims and ideals.

We have accustomed ourselves to think of the present as the Age of Iron, as indeed it is, for we see in the dull grey metal the plastic medium out of which the engineer has modelled the machines and structures which play so large a part in the active life of to-day. Had iron not been at once plentiful and cheap, had it not brought into the hands of the engineer and artificer its marvellous qualities of hardness and softness, of rigidity and toughness, and to the electrician its mysterious and unique magnetic qualities, it is not difficult to conceive that man's control over the forces of Nature might have been delayed for centuries, or perhaps for ages. For iron has been man's chief material instrument in the conquest of Nature; without it the energy alike of the waterfall and of the coalfield would have remained uncontrolled and unused. In this conquest of the resources of Nature for the service of man are we not entitled to say that the intellectual and social gains have equalled, if they have not exceeded, in value the purely

material gains; and may we not then regard iron as the symbol of a beneficent conquest of Nature?

With the advent of the Industrial Age gold was destined to take a new place in the world's history as the great medium of exchange, the great promoter of industry and commerce. While individual gain still remained the propelling power towards its discovery and acquisition, every fresh discovery led directly or indirectly to the freer interchange of the products of industry, and thus reacted favourably on the industrial and social conditions of the time.

So long as the chief supplies of gold were obtained from alluvial deposits by the simple process of washing, the winning of gold almost necessarily continued to be pursued by individuals, or by small groups of workers, who were mainly attracted by the highly speculative nature of the occupation. These workers endured the greatest hardships and ran the most serious personal risks, drawn on from day to day by the hope that some special stroke of good fortune would be theirs. This condition prevailed also in fields in which the reef gold occurred near the surface, where it was easily accessible without costly mining appliances, and where the precious metal was loosely associated with a weathered matrix. These free-milling ores could be readily handled by crushing and amalgamation with mercury, so that here also no elaborate organisation and no great expenditure of capital were necessary. A third stage was reached when the more easily worked deposits above the water-line had been worked out. Not only were more costly appliances and more elaborately organised efforts required to bring the ore to the surface, but the ore when obtained contained less of its gold in the easily recovered, and more in the refractory or combined form. The problem of recovery had now to be attacked by improved mechanical and chemical methods. The sulphides or tellurides with which the gold was associated or combined had to be reduced to a state of minute sub-division by more perfect stamping or grinding, and elaborate precautions were necessary to ensure metallic contact between the particles of gold and the solvent mercury. In many cases the amalgamation process failed to extract more than a very moderate proportion of the gold, and the quartz sand or "tailings" which still contained the remainder found its way into creeks and rivers or remained in heaps on the ground around the batteries. In neighbourhoods where fuel was available a preliminary roasting of the ore was resorted to, to oxidise or volatilise the base metals and set free the gold; or the sulphides, tellurides, &c., were concentrated by washing, and the concentrates were taken to smelting or chlorinating works in some favourable situation where the more elaborate metallurgical methods could be economically applied. Many efforts were also made to apply the solvent action of chlorine directly to the unconcentrated unroasted ores; but unfortunately chlorine is an excellent solvent for other substances besides gold, and in practice it was found that its solvent energy was mainly exercised on the base metals and metalloids, and on the materials of which the apparatus itself was constructed.

This to the best of my knowledge is a correct, if rather sketchy, description of the state of matters in 1889 when the use of a dilute solution of cyanide of potassium was first seriously proposed for the extraction of gold from its ores. Those of us who can recall the time will remember that the proposal was far from favourably regarded from a chemical point of view. The cost of the reagent, its extremely poisonous nature, the instability of its solutions, its slow action—such were the difficulties that naturally presented themselves to our minds. And, even granting that these difficulties might be overcome, there still remained the serious problem of how to recover the gold in metallic form from the extremely dilute solutions of the cyanide of gold and potassium. How each and all of these difficulties have been swept aside, how within little more than a decade this method of gold extraction has spread over the gold-producing countries of the world, now

absorbing and now replacing the older processes, but ever carrying all before it—all this is already a twice-told tale which I should feel hardly justified in alluding to were it not for the fact that we are to-day meeting on the Rand where the infant process made its début nearly fourteen years ago. The Rand to-day is the richest of the world's goldfields, not only in its present capacity, but in its potentialities for the future; twenty years ago its wonderful possibilities were quite unsuspected even by experts.

It is not for me to describe in detail how the change has been accomplished; this task will, we know, be far better accomplished by representative chemists who are now actively engaged in the work. But for the chemists of the British Association it is a fact of great significance that they are here in the presence of the most truly industrial development of gold production which the world has yet seen; a development, moreover, that is founded on a purely chemical process which for its continuance requires, not only skilled chemists to superintend its operation, but equally skilled chemists to supply the reagent on which the industry depends.

In 1889, the world's consumption of cyanide of potassium did not exceed fifty tons per annum. This was produced by melting ferrocyanide with carbonate of potassium, the clear fused cyanide so obtained being decanted from the carbide of iron which had separated. The resulting salt was a mixture of cyanide, cyanate, and carbonate which was sometimes called cyanide of potassium for the hardly sufficient reason that it contained 30 per cent of that salt. When the demand for gold extraction arose, it was at first entirely met by this process, the requisite ferrocyanide being obtained by the old fusion process from the nitrogen of horns, leather, &c. In 1891, the first successful process for the synthetic production of cyanide without the intervention of ferrocyanide was perfected, and the increasing demand from the gold mines was largely met by its use. At present the entire consumption of cyanide is not much short of 10,000 tons a year, of which the Transvaal gold-field consumes about one-third. Large cyanide works exist in Great Britain, Germany, France, and America, so that a steady and sure supply of the reagent has been amply provided. In 1894, the price of cyanide in the Transvaal was 2s. per pound; to-day it is one-third of that, or 8d. During the prevalence of the high prices of earlier years the manufacture was a highly speculative one, and new processes appeared and disappeared with surprising suddenness, the disappearance being generally marked by the simultaneous vanishing of large sums of money. To-day the manufacture is entirely carried out in large works scientifically organised and supervised, and, both industrially and commercially, the speculative element has been eliminated.

Chemistry has so often been called on to play the part of the humble and unrecognised handmaiden to the industrial arts that we may perhaps be pardoned if in this case we call public attention to our Cinderella as she shines in her rightful position as the genius of industrial initiation and direction.

To this essentially chemical development of metallurgy we owe it that in a community whose age can only be counted by decades we find ourselves surrounded by chemists of high scientific skill and attainments who have already organised for their mutual aid and scientific enlightenment "The Johannesburg Society of Chemistry, Metallurgy, and Mining," whose published proceedings amply testify to the atmosphere of intellectual vigour in which the work of this great industry is carried on.

It appears, then, that while gold still maintains its position of influence in the affairs of men, the nature of that influence has undergone an important change. Not only has its widespread use as the chief medium of exchange exercised far-reaching effects on the commerce of the world, but the vastly increased demand for this purpose has in its turn altered the methods of production. These methods have become more highly organised and scientific, and gold production is now fairly established as a progres-

sive industry in which scope is found for the best chemical and engineering skill and talent.

The experience of more highly evolved industries in the older countries has shown that the truly scientific organisation of industry includes in its scope a full and just consideration for the social and intellectual needs of its workers from highest to lowest. It augurs well, therefore, for the future of the gold industry, from the humane and social points of view, that its control should be more and more under the influence of men of scientific spirit and intellectual culture who we may feel assured will not forget the best traditions of their class.

The application of science to industry requires on the part of the pioneers and organisers keen and persistent concentration on certain well-defined aims. Any wavering in these aims or any relaxation of this concentration may lead to failure or to only a qualified success. This necessary but narrow concentration may be a danger to the intellectual development of the worker, who may thereby readily fall into a groove, and so may become even less efficient in his own particular work. It certainly requires some mental strength to hold fast to the well-defined practical aim while allowing to the attention occasional intervals of liberty to browse over the wide and pleasant fields of science. But I am certain that the acquirement of this double power is well worth an effort. The mental stimulus, as well as the new experiences garnered during the excursion, will sooner or later react favourably on the practical problems, while the earnest wrestling with these problems may develop powers and intuitions which will lend their own charm to the wider problems of science.

Gold and Science.

If we re-peruse the table of the elements, not now in our capacity as "plain men" but as chemists, we shall certainly not select gold as of supreme interest chemically. Its position as chief among the noble metals, its patent of nobility, is based on its aloofness from common associations or attachments. Unlike the element nitrogen, it is mainly for itself, and little if at all for its compounds, that gold is interesting. In it we can at our leisure study the *metal* rather than the *element*. Its colour and transparency, its softness and its hardness, the density as well as the extreme tenuity of some of its forms—such were the qualities which recommended it to Faraday when he desired to study the action of material particles on light. I should like to repeat to you in his own words the reasons he gave for this choice:—"Because of its comparative opacity among bodies, and yet possession of a real transparency; because of its development of colour both in the reflected and transmitted rays; because of the state of tenuity and division which it permitted with the preservation of its integrity as a metallic body; because of its supposed simplicity of character; and because known phenomena appeared to indicate that a mere variation in the size of its particles gave rise to a variety of resultant colours. Besides the waves of light are so large compared to the dimensions of the particles of gold which in various conditions can be subjected to a ray, that it seemed probable that the particles might come into effective relations to the much smaller vibrations of the other particles."

I may remind you that Faraday came to the conclusion that the variety in the colours presented by gold under various conditions is due to the size of its particles and their state of aggregation. Ruby glass or ruby solutions he proved are not true solutions, nor are they molecular diffusions of gold, but they contain the metal in aggregates sufficiently large to give a sensible reflection under an incident beam of light. Through the kindness of Sir Henry Roscoe I am able to exhibit to you some of the original ruby gold preparations obtained during this research, which were afterwards presented to him by Faraday at the Royal Institution some years before his death.

By means of refined and ingenious optical methods,

Zigsimondy and Siedentopf have succeeded in making these ultra-microscopic particles visible in the microscope as diffraction discs; they have, further, counted the number of particles per unit area, and have from the intensity of their reflection calculated their size. In ruby glass the size of the particles in different specimens was found to vary from $\frac{1}{4}$ to $\frac{7}{10}$ millionths of a millimetre. No relation was found to hold between the colour of the particles and their absolute size. This conclusion is in direct contradiction of Faraday's belief already referred to. Mr. J. Maxwell Garnett has recently shown that the colour of metallic glasses and films is determined, not only by the absolute size of the metal particles, but also by the proportion of the total volume they occupy in the medium in which they are diffused. The results of Mr. Garnett's calculations are in close agreement with a number of the observations on the colour and micro-structure of thin metal films which I had already recorded, and they appear to me to supply the explanation of much that had appeared puzzling before. My own observations lead me to think that the actual microscopic particles which are to be seen, and the larger of which can also be measured, in films and solutions or suspensions, do not in any way represent the ultimate units of structure which are required by Mr. Garnett's theory, but that these particles are aggregates of smaller units built up in more or less open formation.

That a relatively opaque substance like gold may be so attenuated that when disseminated in open formation it becomes transparent, is contrary to all our associations with the same operation when performed on transparent substances like glass or crystalline salts. The familiar experiment of crushing a transparent crystal into a perfectly opaque powder would not prepare us for the effect of minute sub-division on the transparency of metals. At first it might be supposed that this difference is due to the very rough and incomplete sub-division of the crystal by crushing; but this is not the case, for the perfectly transparent oxide of magnesium may be obtained in a state of attenuation comparable with that of the gold, by allowing the smoke from burning magnesium to deposit on a glass plate. The film of oxide obtained in this way is found to be built up of particles quite as minute as those of which the gold films are composed, yet the opacity of the oxide film is relatively much greater. The minute particles of the dielectric, magnesium oxide, scatter and dissipate the light waves by repeated reflection and refraction, while the similar particles of the metallic conductor, gold, act as electrical resonators which pass on some of the light waves while reflecting others. Specimens of films of gold and silver and of magnesium oxide are exhibited on the table and on the lantern screen. When the metallic particles are in this state of open formation and relative transparency, it was found that the electrical conductivity of the films had completely disappeared. Films of this description were found to have a resistance of over 1,000,000 megohms as compared with only six ohms in the metallic reflecting condition.

Molecules in the Solid State.

My examination of gold films and surfaces has revealed the fact that during polishing the disturbed surface film behaves exactly like a liquid under the influence of surface tension. At temperatures far below the melting-point molecular movement takes place under mechanical disturbance, and the molecules tend to heap up in minute mounds or flattened droplets. These minute mounds are often so shallow that they can only be detected when the surface is illuminated by an intense, obliquely incident beam of light. I have estimated that these minute mounds or spicules can be seen in this way in films which are not more than five to ten micro-millimetres in thickness. A film of this attenuation may contain so few as ten to twenty molecules in its thickness.

When moderately thin films of gold are supported on glass, and heated at a temperature of 400–500°, they become translucent, and the forms assumed under the influence of surface tension can be readily seen by trans-

mitted light. It was in this way that the beautiful but puzzling spicular appearance by obliquely reflected light was first explained as due to the granulation of the surface under the influence of surface tension. Photo-micrographs of these films are exhibited.

Turning now to the mechanical properties of metals, we find that gold has proved itself of great value in the investigation of some of these. It has long been recognised as the most malleable and ductile of the metals, whilst its chemical indifference tends to preserve it in a state of metallic purity throughout any prolonged series of operations.

The artificers in gold must very early have learned that its malleability and ductility are not qualities which indefinitely survive the operations of hammering and wire-drawing. A piece of soft gold beaten into a thin plate does not remain equally soft throughout the process, but spreads with increasing difficulty under the hammer. If carelessly beaten it may even develop cracks round its edges. We may assume that the artificers in gold very soon discovered that by heating, the hardened metal might be restored to its former condition of softness.

In connection with the study of the micro-metallurgy of iron and steel during recent years it has been recognised that heat annealing is, as a rule, associated with the growth and development of crystalline grains, and Professor Ewing and Mr. Rosenhain have shown that overstrain is often if not invariably associated with the deformation of these crystalline grains by slips occurring along one or more cleavage planes. This hypothesis, though well supported up to a point by microscopic observations on a variety of metals, offers no explanation of the natural arrest of malleability or ductility which occurs when the overstrain has reached a point at which the crystalline grains are still, to all appearance only, slightly deformed. At this stage there is no obvious reason why the slipping of the crystalline lamellæ should not continue under the stresses which have initiated it. But far from this being the case, a relatively great increase of stress produces little or no further yielding till the breaking point is reached and rupture takes place.

The study of the surface effects of polishing, already referred to, had shown that the thin surface film retained no trace of crystalline structure; while it also gave the clearest indications that the metal had passed through a liquid condition before settling into the forms prescribed by surface tension. From this it was argued that the conditions which prevail at the outer surface might equally prevail at all inner surfaces where movement had occurred, so that every slip of one crystalline lamella over another would cause a thin film of the metal to pass through the liquid phase to a new and non-crystalline condition. By observations on the effects of beating pure gold foil, it was found that the metal reached its hardest and least plastic condition only when all outward traces of crystalline structure had disappeared. It was also ascertained that this complete destruction of the crystalline lamellæ and units could only be accomplished in the layers near the surface, for the hardened substance produced by the flowing under the hammer appears to encase and protect the crystalline units after they become broken down to a certain size. By carefully etching the surface in stages by means of chlorine water or cold aqua regia, the successive layers below the surface were disclosed. The surface itself was vitreous; beneath this was a layer of minute granules, and lower still the distorted and broken-up remains of crystalline lamellæ and grains were embedded in a vitreous and granular matrix. The vitreous-looking surface layer represents the final stage in the passage from soft to hard, from crystalline to amorphous. By heating the beaten foil, its softness was restored; and on etching the annealed metal it was found that the crystalline structure also was fully restored. Photomicrographs showing these appearances are exhibited. These microscopic observations were fully confirmed by finding well-marked thermo-electrical and electro-chemical distinctions

between the two forms of metal, the hard and soft or the amorphous and the crystalline. The determination of a definite transition temperature at which the amorphous metal passes into the crystalline metal further confirms the phase view of hardening by overstrain and softening by annealing.

It was subsequently proved that *the property of passing from crystalline to amorphous by mechanical flow, and from amorphous to crystalline by heat at a definite transition temperature, is a general one which is possessed by all crystalline solids which do not decompose at or below their transition temperature.* The significance of this fact I venture to think entitles it to more than a passing reference. It appears to me to mean that the transition from amorphous to crystalline is entitled to take its place with the other great changes of state, solid to liquid, liquid to gas, for like these it marks a change in the molecular activity which occurs when a certain temperature is reached. It is entitled to take this place because there is every indication that the change is as general in its nature as the other changes of state. Compare it, for instance, with the allotropic changes with which chemists have been familiar. These are for the most part changes which are special to particular elements or compounds, and are usually classed with the chemical properties by which the substances may be distinguished from each other. Very different is the amorphous crystalline change, for although in particular cases it may have been observed and associated with allotropic changes, yet the causes of its occurrence are more deeply founded in the relations between the molecules and the heat energy by which their manifold properties are successively unfolded as temperature is raised from the absolute zero. At this transition-point we find ourselves face to face with the first stirrings of a specific directive force by which the blind cohesion of the molecules is ordered and directed to the building up of the most perfect geometric forms. It is hardly possible any longer to regard the stability of a crystal as static and inert, and independent of temperature; rather must its structure and symmetry be taken as the outward manifestation of a dynamic equilibrium between the primitive cohesion and the kinetic energy imparted by heat. Even before the discovery of a definite temperature of transition from the amorphous to the crystalline phase we had in our hands the proofs that in certain cases the crystalline state can be a state of dynamic, rather than of static equilibrium. The transition of sulphur from the rhombic to the prismatic form supplies an example of crystalline stability which persists only between certain narrow limits of temperature. Within these limits the crystal is a "living crystal" if one may borrow an analogy from the organic world. It can still grow, and it will under proper conditions repair any damage it may receive.

The passage of the same substance through several crystalline phases, each only stable over a limited range of temperature, strongly supports the general conclusion drawn from the existence of a stability temperature between the amorphous and crystalline phases, namely, that the crystalline arrangement of the molecules requires for its active existence the particular kind or rate of vibration corresponding with a certain range of temperature. Below this point the crystal may become to all appearance a mere pseudomorph with no powers of active growth or repair. But these powers are not extinct—they are only in abeyance ready to be called forth under the energising influence of heat. This temporary abeyance of the more active properties of matter is strikingly illustrated by the early observations of Sir James Dewar at the boiling-point of liquid air, and more recently at that of liquid hydrogen. At the latter temperature even chemical affinity becomes latent. In metals it was found that the changes in their physical properties brought about by these low temperatures are not permanent, but only persist so long as the low temperature is maintained. During the past year Mr. R. A. Hadfield has supplemented these earlier results by making a very complete series of observations on the effect

of cooling on the mechanical properties of iron and its alloys. The tenacity and hardness of the pure metal and its alloys at the ordinary temperature and at -182° have been compared, and it has been found that these qualities are invariably enhanced at the lower temperature, but that they return exactly to their former value at the ordinary temperature. By the mere abstraction of heat between the temperatures of 18° and -182° the tensile strength of pure metals is raised 50 to 100 per cent. In pure iron the increase is from 23 tons per square inch at 18° C. to 52 tons at -182° ; in gold from 15.1 tons to 22.4 tons; and in copper from 19.5 tons to 26.4. This increase is not, I think, due to the closer approximation of the molecules, for the coefficient of expansion of most metals below 0° is extremely small. Neither is it due to permanent changes of molecular arrangement or aggregation, for Mr. Hadfield has obtained a perfectly smooth and regular cooling curve for iron between 18° and -182° , and there appears to be no indication of the existence of any critical point between these temperatures. Further, the complete restoration of the original tenacity on the return to the higher temperature shows that no permanent or irreversible change has occurred during cooling. Everything therefore indicates that the increase of tenacity which occurs degree by degree as heat is removed is due to the reduction of the repulsive force of molecular vibration, so that the primary cohesive force can assert itself more and more completely as the absolute zero is approached.

The metals experimented with by Mr. Hadfield were all in the annealed or crystalline condition, so that the molecules must have exerted their mutual attractions along the directed axes proper to this state. It is to be expected that similar experiments with the metals in the amorphous state may throw light on the question whether and to what extent the crystalline state depends on a dynamic equilibrium between the forces of cohesion and repulsion, or whether a directed cohesion exists fully developed in the molecules at the absolute zero.*

The phenomena of the solid state throw an interesting light on the interplay of the two great forces, the primitive or blind cohesion which holds undisputed sway at the absolute zero, and the repulsion due to the molecular vibrations which is developed by heat. This interplay we know continues through the states which succeed each other as the temperature is raised, till a point is reached at which the molecular repulsions so far outweigh the cohesive force that the substance behaves like a perfect gas. The problems of molecular constitution are more likely to be elucidated by a study of the successive states between the absolute zero and the vaporising temperature than at the upper ranges where the gaseous state alone prevails. The simplicity of the laws which govern the physical behaviour of a perfect gas is very attractive, but we must not forget that this simplicity is only possible because repulsion has so nearly overcome cohesion that the latter may be practically ignored. The attractiveness of this simplicity should not blind us to the fact that it is in the middle region, where the opposing forces are more nearly equal, that the most interesting and illuminating phenomena are likely to abound. The application of the gas laws to the phenomena of solution and osmosis appears to be one of those cases in which an attractive appearance of simplicity in the apparent relations may prove very misleading.

Before passing from the specially metallic qualities of gold I will only remind you of the important part it has played in the researches on the diffusion of metals by the late Sir William Roberts-Austen, and in those of Mr. Haycock and Mr. Neville on the freezing-points of solutions of gold in tin, which led to the recognition of the monatomic nature of the molecules of metals.

* Since the above was written a series of observations has been made on the influence of low temperature on the tenacity of pure metals in the amorphous condition. These observations will form the subject of a separate communication to the Section.

Molecules in Solution.

It has occurred to me that the practice of the cyanide process of gold extraction presents us with several new and interesting aspects of the problems of solution. As you are aware, the gold is first obtained from the ore in the form of a very dilute solution of cyanide of gold and potassium from which the metal has to be separated, either by passing it through boxes filled with zinc shavings, or by electrolysis in large cells.

The solution as it leaves the cyanide-vats may contain gold equal to 100 grains or more per ton, and as it leaves the precipitating-boxes it may contain as little as 1 or 2 grains and as much as 20 grains. In the treatment of slimes much larger volumes of solution have to be dealt with, and in this case solutions containing 18 grains per ton have been regularly passed through the precipitating-boxes, their gold content being reduced to $1\frac{1}{2}$ grains per ton. In round numbers we may say that 1 gm. of gold is recovered from 1 cubic metre of solution, while 0.1 gm. is left in the solution. Even from the point of view of the physical chemist we are here in presence of solutions of a very remarkable order of dilution. A solution containing 1 gm. per cubic metre is in round numbers N/200,000, and the weaker solution containing 0.1 gm. is N/2,000,000. It is convenient to remember that the latter contains a little more than $1\frac{1}{2}$ grains per ton. In experiments on the properties of dilute solutions the extreme point of dilution was reached by Kohlrausch, who employed solutions containing 1/100,000 of a gm. molecule of solute per litre for his conductivity experiments. These solutions were therefore twice as strong as the gold solution with 1 gm. per cubic metre, and twenty times as strong as the more dilute solution. This fact must be my excuse for placing before you the results of a few simple calculations as to the molecular distribution in these solutions, which have certainly given me an entirely new view of what constitutes a really dilute solution from the molecular point of view.

In estimating the number of molecules in a given volume of solution the method adopted is to divide the space into minute cubical cells, each of which can exactly contain a sphere of the diameter of the molecule. In this way a form of piling for the molecules is assumed which, though not the closest possible, may quite probably represent the piling of water molecules. Taking the molecular diameter as 0.2×10^{-6} millimetres—a figure which is possibly too small for the water molecules and too large for the gold—it is found that a cubic millimetre of solution contains 125×10^{18} molecules, or 125 quadrillions. The head of an ordinary pin, if it were spherical, would have a volume of about 1 cubic millimetre.

If these water molecules could be arranged in a single row, each molecule just touching its two nearest neighbours, the length of the row would be 25,000,000 kilometres. A thread of these fairy beads, which contained the molecules of one very small drop of a volume of 6 cubic millimetres, would reach from the earth to the sun, a distance of about 150,000,000 kilometres.

In a solution containing $1\frac{1}{2}$ grains of gold per ton, or 1 decigram. per cubic metre, the ratio of gold molecules to water molecules is as 1:193,000,000. Each cubic millimetre of the solution therefore contains 6,500,000,000 gold molecules. If these are uniformly distributed throughout the solution each will be about 400 micro-millimetres, or 1/60,000 of an inch, from its nearest neighbours. This is not really very wide spacing, for the point of the finest sewing-needle would cover about 1500 gold molecules.

If a cubic metre of solution could be spread out in a sheet one molecule in thickness it would cover an area of 1680 square miles, and nowhere in this area would it be possible to put down the point of the needle without touching some hundreds of gold molecules simultaneously.

According to Professor Liversidge, sea-water contains on the average about 1 grain of gold per ton. If this is the case, then the above figures for the dilute cyanide solution apply with only a slight modification to sea-water. No drop, however small it may be, can be removed from the

ocean which will not contain many millions of gold molecules, and no point of its surface can be touched which is not thickly strewn with these. From this molecular point of view we must realise that our ships literally float on a gilded ocean!

From time to time adventurers arise who attempt to launch upon this gilded ocean unseaworthy ships freighted with the savings of the trusting investor. In order that nothing which has been said here may tempt anyone to contribute to the freighting of these ships, let me hasten to point out that the weakest of the cyanide solutions here referred to is richer in gold than sea-water is reported to be. The practical conclusion from this comparison is sufficiently obvious. If the cyaniding expert, whose business it is to extract gold from dilute solutions, finds that it does not pay to carry this extraction beyond a concentration of 2 or 3 grains per ton, even when the solution is already in his hand, and when therefore the costs of treatment are at their minimum, how can it possibly pay to begin the work of extraction on sea-water, a solution of one-half the richness, which would have to be impounded and treated by methods which could not fail to be more costly in labour and materials than the simple process of zinc-box precipitation? It is generally unsafe to prophesy, but in this case I am rash enough to risk the prediction that if ever the gold mines of the Transvaal are shut up it will not be owing to the competition of the gold resources of the ocean.

In these calculations with reference to the dilute cyanide solutions it is assumed that the gold molecules are uniformly distributed, that they are practically equidistant from each other. There appears to me to be considerable doubt whether we have any right to make this assumption. Leaving out of account for the moment the action of the water molecules, it would appear that as long as the gold molecules are so numerous that a uniform distribution would bring them within the range of each other's attraction, we can imagine that all submerged molecules would be in equilibrium so far as the attractions of their own kind are concerned, being subjected to a uniform pull in all directions. This condition would certainly make for uniform distribution. But when the distance between them exceeds the range of the molecular forces, it is evident that an entirely new condition is introduced, and it seems not improbable that the widely distributed molecules would tend to drift into clouds in which they are brought back within the range of these forces. The range of the cohesive forces in water and aqueous liquids is usually taken from 50 to 100 micro-millimetres, and I am disposed to think that ten times this amount would not be an excessive estimate of the range in the case of gold. If the range for gold be taken as 500 micro-millimetres, then the gold molecules of the dilute gold solution, which are spaced at 400 micro-millimetres apart, are just within the range of each other's attraction, and their distribution is therefore likely to be uniform. But by a further dilution to half concentration, the equilibrium would be liable to be disturbed, and denser clouds of gold molecules would be formed, with less dense intervals between them.

In preparing the zinc boxes through which the gold solution is passed, very great care has to be exercised to ensure that the contact surface of the zinc is used to the best advantage. With this object the packing of the zinc shavings is so managed that the solution is spread over the zinc surface in as thin sheets as possible. The object, of course, is to bring as many of the gold molecules as possible into actual contact with the zinc. The gold molecules found in the solution leaving the boxes are those which have not been in contact with the zinc. Yet we have seen that these molecules are still so numerous that they are within 1/60,000 of an inch of each other. If these molecules are in a state analogous to the gaseous state, with diffusive energy of the same order as that of the gas molecule, it is difficult to imagine how they can escape without coming in contact with the zinc surface during their tortuous passage through the boxes and being deposited there. Yet they do escape, even when the

velocity of the solution in passing over the zinc surfaces is so slow as 10 c.m. per minute, or 1.6 m.m. per second.

We may regard the condition of these isolated gold molecules, or the more complex auricyanide of potassium molecules, as typical of that of the solute molecules in a dilute solution of any non-volatile solid. They are solid molecules sparsely distributed among a multitude of intensely active solvent molecules, the temperature of the solution being many hundred degrees below that at which they could of themselves assume the greater freedom of the liquid or gaseous state. These solute molecules have to a great extent been set free from the constraining effect of their cohesive forces, but it is important to remember that *this freedom has not been attained by the increase of their own kinetic energy as in liquefaction by heat.* Their freedom and the extra kinetic energy they have acquired have in some way been imparted to them by the more active solvent molecules; for, if the solvent could be suddenly removed, leaving the solute molecules still similarly distributed in a vacuous space, they would eventually condense into a solid aggregate. This must be the case, for the non-volatile solute has no measurable vapour pressure at the temperature of the solution. The kinetic energy of the solute molecules is of itself quite insufficient to endow them with the properties of the gaseous or even of the liquid molecule, even when their cohesive forces have been weakened or overcome by separation.

If the energy employed in this separation is not intrinsic to the solute molecule then it must in some way have been imparted by the solvent molecules. It therefore becomes important to compare the energy endowment of one set of molecules with that of the other.

Compared with other solids, ice at its freezing-point has very little hardness or tenacity; the cohesion of its molecules has been much relaxed by the great absorption of heat energy between the absolute zero and the freezing-point. If an average specific heat of 0.5 over the whole range be assumed, the heat absorption of 1 gm. amounts to 136.5 calories. In the transition to the liquid state at 0° a further absorption of 79 calories takes place, so that a gm. of liquid water at the freezing-point contains the heat energy of 215.5 calories. The fact that water has the high vapour pressure of 4.6 m.m. of mercury at the freezing-point is probably a result of this enormous store of energy. As a liquid, therefore, it is natural to expect that its molecules will exhibit effects proportionate to this great store of energy. This expectation appears to be realised when we consider, not only its properties as the universal solvent, but its osmotic and diffusive energy in solutions in which it is the solvent.

To complete the comparison it is only necessary to calculate the heat energy of gold at 0°. Taking its specific heat as 0.032, a gm. of gold at 0° contains 8.7 calories. A gm.-molecule, therefore, contains in round numbers 1700 calories, as compared with 3880 calories in a gm.-molecule of water.

Taking into consideration not only this greater store of energy, but also the much smaller cohesive force of water as compared with the majority of solid solutes, there can be no doubt that the active rôle in aqueous solutions of this type must be assigned to the solvent, not to the solute molecules.

This leads to the important conclusion that the energy of solution, of diffusion, and of osmosis is due, not to the imaginary gaseous energy of the solute, but to the actual kinetic energy of the solvent molecules. When this conclusion is reached a new physical explanation of these phenomena is in our hands, and we are relieved from the strain to the imagination involved in the application of the gas theory to solutions of non-volatile solids.

This transference of the active rôle to the solvent molecules does not in any way affect the well-established conclusions based on the laws of thermodynamics as to the energy relations in these phenomena, for it has always been recognised that these conclusions have reference to the average conditions prevailing in large collections of

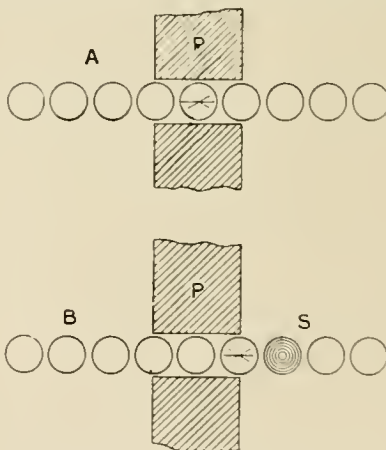
relatively minute units. Wherever the gas analogy has appeared to hold it has not necessarily involved more than this, that the observed effects are in proportion to the number of these minute units in a given volume.

In applying the gas theory to the physical explanation of osmotic pressure, it has been the custom to regard this pressure as directly due to the bombardment of the semi-permeable membrane by the solute molecules. But this conception completely ignores the fact that the pressure developed is a hydrostatic—not a gaseous—pressure, and that the hydrostatic pressure results directly from the *penetration of the solvent molecules from the other side of the partition.*

It appears to me more natural to abandon the gas analogy altogether, to regard the molecules as in the solid and liquid condition proper to their temperature, and to apportion to them their respective parts in the active changes according to their obvious endowment of energy.

Applying this view to the case of a solution and a solvent separated by a semi-permeable membrane, it is seen that the pressure rises on the solution side, because the pure solvent molecules on the other side have some advantage for the display of their energy over the similar molecules in the solution. *This effect, in its most general form, may be attributed to the dilution of the solvent by the solute molecules.* In cases where the osmotic pressure appears to obey Boyle's law, the effect is exactly measured by the number of solute molecules per unit volume. But the facts of this position are in no way changed if the effect is taken to be due to the activity of an equal number of solvent molecules, for we then see that each solute molecule, by cancelling the activity of one solvent molecule on the solution side, permits a solvent molecule from the other side to enter the solution.

What the exact mechanism of this cancellation is there is at present no evidence to show, and the caution originally given by Lord Kelvin with reference to the undue forcing of the gas analogy must also be applied to the suggestion now put forward. But as a means of making the suggestion a little more clear I give here a simple diagram



on which A represents a single perforation in a semi-permeable membrane, P, on both sides of which there is only pure solvent. For the sake of clearness, the molecules are shown only as a single row. Normally there will be no passage of solvent molecules from side to side, for the average kinetic energy of the molecules on both sides is equal. This state of equilibrium is indicated on the diagram by marking with a cross the molecule which is exactly halfway through the partition.

At a single solute molecule, S, has been introduced at the right side. If this molecule exactly cancels the energy of one solute molecule at its own end of the row, the equi-

brium point will move one molecule to the right, the solvent molecules will move in the same direction, and one of their number will enter on the solution side. So long as the row includes one, and only one, solute molecule, the equilibrium will remain unchanged and no more solute molecules will pass in. If another solute molecule arrives on the scene, the equilibrium will again be disturbed in the same way as before, and another solvent molecule will pass into the solution.

This mechanism accomplishes to some extent the work of a "Maxwell Demon," in so far at least as it takes advantage of the movement of *individual molecules* to raise one part of a system at a uniform temperature to a higher level of energy.

A Mechanical View of Dissociation in Dilute Solutions.

The view that the phenomena of solution depend on the relative kinetic energy of the solvent and solute molecules appears to apply with special force to the phenomena of dissociation in dilute solutions. Under the gas theory there does not appear to be any reason why the solute molecules should dissociate into their ions. So obvious is this absence of any physical motive that Professor Armstrong has happily referred to the dissociation as "the suicides of the molecules." Others have proposed to ascribe the phenomenon to what might be called "the fickleness of the ions," thus supposing that the ions have an inherent love of changing partners. These may be picturesque ways of labelling certain views of the situation, but the views themselves do not appear to supply any clue to the physical nature of the phenomena. With the acceptance of the view that the phenomena of solution are largely due to the kinetic energy of the solvent molecules, the phenomena of dissociation also appear to take their place as a natural result of this activity. For consider the situation of an isolated molecule of cyanide of gold and potassium closely surrounded by and at the mercy of some millions of water molecules all in a state of intense activity. The rude mechanical jostling to which the complex molecule is subjected will naturally tend to break it up into simpler portions which are mechanically more stable. The mechanical analogy of a ball mill in which the balls are self-driven at an enormous velocity is probably rather crude, but it may at least help us to picture what, on the view now advanced, must be essentially a mechanical operation.

In importing this mechanical view of the breaking down of complex into simpler molecules we are not without some solid basis of facts to go upon. My own observations have shown that even in the solid state the crystalline molecule can be broken down by purely mechanical means into the simpler units of the amorphous state; and, further, that the water molecules of a crystal may by the same agency be broken away from their combination with the salt molecules. Since the publication of the earlier of these observations Professor Spring has shown that the acid sulphates of the alkali metals may be mechanically decomposed into two portions, one of which contains more acid, and the other more base than the original salt. It is important to recognise that in these three apparently short steps the transition has been made from the overcoming of the simple cohesion of similar molecules in contact with each other to the breaking asunder of the chemical union of dissimilar molecules. At each step the solid molecules appear, not as mere ethereal abstractions, but as substantial portions of matter which can be touched and handled mechanically.

The physical properties of a gas are primarily due to its being an assemblage of rapidly moving molecules. These simpler and more general properties can coexist with, and may be modified by, the more complex relations introduced by chemical affinity as it occurs in compound gases and mixtures.

It appears to me quite legitimate similarly to regard the physical properties of a *liquid* as due to its being an assemblage of rapidly moving molecules. The liquid system is

highly condensed, and the motions of its molecules are controlled by the cohesive as well as by the repulsive forces. The closer approximation of the molecules may reduce their mean free path to an extremely small amount, or it may even cause their translatory motion to disappear, so that the whole kinetic energy of the liquid molecules may be in the form of rotation or vibration.

As we can imagine a perfect gas, so also may we imagine a perfect liquid, the physical properties of which are as simply related to the laws of dynamics as are those of the gas. But the conditions of the liquid state being also those most favourable to the play of chemical affinity, the internal equilibrium of solutions or of mixed liquids must be a resultant of this affinity together with the primary forces of the ideal liquid state.

An ideally perfect solution—that is, a solution the physical properties of which are determined solely by the number of molecules it contains in a given volume—must consist of a solvent and a solute which have no chemical affinity for each other, so that their molecules will neither associate nor dissociate in solution. Probably only comparatively few solutions will be found which even approximate to this ideal perfection. But it appears to me that the study of the problems of the liquid and the dissolved states may be much simplified by the recognition (1) that the primary physical properties of liquids and solutions are due to the fact that they are assemblages of molecules endowed with the amount and the kind of kinetic energy which is proper to their temperature; and (2) that as these primary physical properties of the liquid and dissolved states may be masked and interfered with by chemical affinity, they should be studied as far as possible in examples where the influence of this force is either absent or at a minimum.

THE "THORIUM ACTIVITY" OF MONAZITE.

By F. GIESEL.

FROM the work of Elster and Geitel on the radio-active constituents of Baden-Baden mud (*Physikal. Zeit.*, 1905, vi., 67) and of Hahn and Sackur on the thoranite from Ceylon (*Berichte*, 1905, xxxviii., 1756) it follows that thorium itself does not seem to produce the emanation named after it.

Accordingly, it is also to be assumed that commercial thorium owes its activity to the presence of traces of an impurity of a far more active substance.

Experiments which I arranged some time ago with an artificial barium sulphate precipitate obtained from monazite cerium liquors (thorium had previously been completely removed) seem to confirm this. This precipitate, which carries down the rare earths with it, had been obtained incidentally two years ago during the working up of 30 k.grms. of monazite sand, and was given to me through the kindness of Herr Przibylla. The activity of the product was about double that of thorium oxalate,* and the decay constant of the induction was identical with that of thorium.

From 1 k.grm., the greater part of the barium sulphate precipitate, the earths, after being converted into chloride, were separated from the barium by means of ammonia; as oxalates they weighed 115 grms. On being converted into chloride a small quantity of sulphate remained behind undecomposed. It appeared that the activity was considerably concentrated in this residue, while that of the 115 grms. had greatly diminished. The ammonia precipitate of the rare earths obtained as above from this

* In the determination of the activity of the preparation in Elster and Geitel's apparatus, just as with emanium preparations, we have to take into account the variations in the power of emanation, which are dependent upon the chemical condition. For example, thorium oxide obtained by igniting the oxalate gave a leakage about five times as great as that of the oxalate. Thorium hydroxide obtained by precipitation with caustic potash at once gave a leakage fifty times as great as that of the oxalate used.

sulphate was decomposed while still moist by means of ammonium carbonate into a soluble portion of 0.1 gm. (as oxalate) and an insoluble portion of 2 grms. (as oxalate).

The latter 2 grms. contained chiefly cerium. After ignition of the oxalates there remained 0.12 gm. undissolved in nitric acid; 0.65 gm. were precipitated with permanganate and magnesia, and the filtrate gave 0.03 gm. of oxalate as the part richest in lanthanum.

The former 0.1 gm. of oxalate must contain the thorium; it was extracted with ammonium oxalate, and gave 6 m.grms. of oxalate residue and 0.04 gm. of hydroxide from the filtrate. The hydroxide might be considered to be thorium.

The examination in the leakage apparatus of the preparations thus separated showed that the further chemical separations had not appreciably affected the activity; they all gave a value about ten times as high as that of thorium hydroxide. The preparations do not excite the luminescent screen, as a barium-radium preparation of equal leakage does, probably because the discharging effect is due essentially to the emanation.

Elster and Geitel have kindly determined the decay constants of the induction of most of the preparations. With the 0.65 gm. of the cerium precipitate the induced activity showed the increase characteristic of thorium, shortly after the end of the exposure. The decay of the emanation itself was also determined, and it was found that it disappears almost entirely in an hour. The physical properties resemble those of the preparation obtained by Elster and Geitel from the Baden-Baden mud.

From these experiments it follows that the "thorium activity" of monazite is not to be ascribed to thorium itself, and that it may even reach a higher value in preparations which are practically free from thorium.

Addendum.—As a supplement to my article in these *Berichte* (1905, xxxviii., 707) it may be mentioned that from cerium earths containing emanium, by repeated crystallisation of the magnesium double nitrates, the lanthanum salt can be obtained free from emanium (thus inactive).

Emanium X can be completely precipitated by means of artificial barium sulphate from neutral chloride solution of the rare earths (free from thorium), so that after precipitation of these earths by ammonia, the presence of EX can no longer be detected either in the hydroxides nor in the filtrate.—*Berichte*, 1905, xxxviii., 2334.

ACTINIUM AND EMANIUM.

By W. MARCKWALD.

It is well known that Debierne (*Comptes Rendus*, 1899, cxxix., 593) discovered in pitchblende a radio-active substance, which follows the reactions of thorium and is characterised by the high power of emanation, and which he called actinium. Afterwards, Giesel (*Berichte*, 1902, xxxv., 3608) found in the rare earths separated from radium mother-liquors a substance which accompanies lanthanum, and which he named emanium on account of its extraordinary power of emanation.

More recently the identity of actinium and emanium was first affirmed by Debierne (*Comptes Rendus*, 1904, cxxxix., 14), and afterwards admitted with certain reservations by Giesel (*Berichte*, 1904, xxxvii., 3963). Finally, Sackur and Hahn (*Berichte*, 1905, xxxviii., 1943) showed that the decay constants of actinium and emanium agreed, and hence they concluded for this reason also that the two substances are identical.

An investigation of the rare earths, which we separated from radium mother-liquors, and 40 grms. of which were placed at my disposal by the firm of Dr. Rich. Sthamer, of Hamburg, most unexpectedly provided an elucidation of this question. These earths, which gave off considerable emanation, were converted into chlorides, and the thorium was separated in the usual way by means of thiosulphate.

There was only a very small quantity of this thorium, amounting to 0.7 gm. It gave off the emanation very strongly, and the emanation showed the characteristic short duration of life, which was not measured accurately. Thus I had obtained a specimen of actinium.

From the solution which had been freed from thorium, the cerium was first separated (by Mosander's method), and then the didymium and lanthanum were together separated as oxalates, and again converted into oxides. Neither the cerium oxide nor the mixture of didymium and lanthanum oxides showed any appreciable power of emanation.

The thorium from the thiosulphate precipitate was again purified by dissolving in hydrochloric acid, precipitated in oxalic acid, and the oxalate was then dissolved in ammonium oxalate. After filtering off the very small residue, the thorium oxalate was precipitated from the solution by acidifying, and converted into oxide by ignition. In all these operations the emanating substance had followed thorium.

By taking observations for several months it was found that this actinium lost its power of emanation as well as its radio-activity. While the cerium oxide preserved its small residual activity during the period mentioned, in the case of the mixture of didymium and lanthanum oxides the power of emanation appeared again at the same rate as it decayed in the case of the thorium oxide, till finally the latter only showed the emanation very slightly, and the didymium-lanthanum oxide, on the contrary, showed it very strongly.

Thus we have a case similar to that which has been completely investigated and explained by the beautiful researches of Rutherford and Soddy on the relation of thorium to thorium X. A radio-active substance follows lanthanum—for didymium according to Giesel's researches is indifferent—and its decay product is a second substance allied to thorium in its chemical reactions. This second substance is further decomposed, giving a strong emanation.

It is easy to show that this view corresponds to the facts. As after a period of some months the mixture of lanthanum and didymium oxides freed from thorium—amounting to 18 grms.—again gave the emanation strongly, it was dissolved in hydrochloric acid together with 0.5 gm. of ordinary thorium oxide, and the thorium was again precipitated with thiosulphate. The precipitate then contained almost all the carrier of the power of emanation, and the didymium-lanthanum oxide mixture again obtained from the solution was only feebly active.

In his most recent article on this subject Giesel (*Berichte*, 1905, xxxviii., 775) has alluded to the existence of an emanium X, which remains in the solution when lanthanum-emanium oxide is precipitated by ammonia. Hence the behaviour of the strongly emanating thorium obtained as above was investigated when it was precipitated with ammonia. It then appeared that the thorium hydroxide thus separated still gave the same strong emanation, while the solution, after it had been evaporated and the ammonium salts had been driven off, left no appreciable emanating residue.

From the foregoing it follows that *actinium and emanium are not identical, but stand in a genetic relation*. Emanium, if we designate thus the substance following lanthanum, produces actinium, the strongly emanating substance following thorium. The name emanium is not at all well chosen, for this substance gives no emanation whatever. It would have been better to name actinium from its power of emanation.

Such unsuitable names would be avoided if all the chemists engaged in research in the province of radio-activity would refrain from naming newly discovered substances until their properties had been thoroughly investigated. If insufficiently characterised substances are provided with names, complication results instead of simplification. Besides the example in question we may call attention to the case of polonium.—*Berichte*, 1905, xxxviii., 2264.

THE OXIDATION OF SULPHITES BY IODINE IN ALKALINE SOLUTION.

By R. HARMAN ASHLEY.

ACCORDING to Bunsen, Dupasquier's method of oxidising sulphurous acid by iodine in an acid solution, proceeds to completion according to the equation $2\text{SO}_2 + 2\text{I}_2 + 4\text{H}_2\text{O} = 4\text{HI} + 2\text{H}_2\text{SO}_4$ only when the concentration of the sulphur dioxide does not exceed 0.5 per cent of the solution. When, on the other hand, the proportion of sulphur dioxide exceeds this value, there is a secondary reaction, which, according to Volhard, involves the reduction of the sulphur dioxide by the hydriodic acid produced. This difficulty may be obviated, however, as has been shown by Volhard (*Ann. Chem.*, ccxlii., 93), if the solution of the sulphurous acid or a sulphite is run (with stirring) into a solution of iodine in potassium iodide, acidified with hydrochloric acid, to the bleaching of colour, using starch as an indicator—a procedure which is obviously less convenient than direct titration by a standard solution of iodine.

It has been recently further proposed by E. Rupp (*Ber.*, xxxv., 3694) to accomplish the oxidation in an alkaline solution, by treating the solution of sulphur dioxide or a sulphite with an excess of standard iodine in presence of acid sodium carbonate (1 grm.) during an interval of fifteen minutes, and determining the excess of iodine with sodium thiosulphate. Rupp's analytical examples, three in number, involving amounts of sulphur dioxide approximating 0.0343 grm., show small errors of excess, and from them the conclusion is drawn that sulphites, like arsenites, may be estimated in a solution made alkaline with sodium bicarbonate by the process indicated.

This very unusual use of sodium thiosulphate for the determination of free iodine in the presence of an alkali bicarbonate, suggests the question as to whether the sulphite was in reality completely oxidised by the treatment, or whether the apparently good results were in fact due to a chance balancing of errors of incomplete oxidation of the sulphite on the one hand, and, on the other hand, of the excessive use of iodine in the action of the thiosulphate in an alkaline solution, it being generally supposed that, in alkaline solutions, not only is the expected tetrathionate formed, but that some of the thiosulphate is oxidised to the extent of forming sulphate rather than tetrathionate exclusively.

In Table I. are data of experiments upon the action of iodine and sodium thiosulphate in alkaline solution. The sodium thiosulphate, approximately N/10, was standardised against approximately N/10 iodine solution in a neutral solution. Varying amounts of a saturated solution of acid sodium carbonate were used to render the solution alkaline in the experiments recorded.

TABLE I.

Iodine solution = 0.01236 grm. per c.c.					
Sodium thiosulphate solution = 0.01516 " "					
No.	Na ₂ S ₂ O ₃ , nearly N/10.		Iodine, nearly N/10.		Error in terms of I.
	C.c.	Grm.	C.c.	Grm.	
1.	11.94	0.1451	15.00	0.1854	+0.0403
2.	11.60	0.1421	15.00	0.1854	+0.0433
3.	11.18	0.1359	15.00	0.1854	+0.0495
4.	11.25	0.1367	15.00	0.1854	+0.0487
5.	9.18	0.1116	11.00	0.1360	+0.0244
6.	9.11	0.1107	11.00	0.1360	+0.0253
7.	15.00	0.1823	15.08	0.1975	+0.0152
8.	15.00	0.1823	16.31	0.2016	+0.0193
9.	15.00	0.1823	16.62	0.2054	+0.0231
10.	15.00	0.1823	16.65	0.2058	+0.0235

Treatment.—Nos. 1—6: Na₂S₂O₃ into iodine. Nos. 7—10: Iodine into Na₂S₂O₃.

It is plainly evident from Table I. that more iodine is used up in the presence of an alkali bicarbonate, whether the iodine is run into the thiosulphate or the thiosulphate into the iodine, than accords with the theory of the reaction.

Experiments were now undertaken for the purpose of contrasting the results obtained by Rupp's procedure with results found by oxidising the sulphite with iodine in an alkaline solution and determining the excess of iodine by standard arsenite, which, as is well known, acts with regularity upon iodine in the presence of an acid sodium carbonate. The volumes of the solutions at the time of oxidation varied from 25 to 50 c.c. The results are given in Table II.

TABLE II.
Rupp's Procedure.

Iodine value of SO ₂ taken.	Iodine taken.	Iodine value of Na ₂ S ₂ O ₃ taken.	NaHCO ₃ taken.	Error in terms of iodine.	Error in terms of SO ₂ .
Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
0.0977	0.2474	0.1492	1	+0.0005	+0.0001
0.0977	0.2474	0.1454	1	+0.0043	+0.0011
0.1440	0.2969	0.1528	1	+0.0001	0.0000
0.1440	0.2969	0.1518	1	+0.0011	+0.0003
0.2759	0.4316	0.1582	1	-0.0025	-0.0006
0.2759	0.4316	0.1628	1	-0.0071	-0.0018

Excess of Iodine Determined by Standard Arsenite.

	Iodine value of arsenite taken.				
0.0977	0.2495	0.1543	1	-0.0025	-0.0006
0.0977	0.2495	0.1510	1	-0.0022	-0.0006
0.1440	0.2984	0.1586	1	-0.0042	-0.0010
0.1440	0.3017	0.1607	1	-0.0030	-0.0008
0.2759	0.4354	0.1710	1	-0.0115	-0.0029
0.2759	0.4354	0.1742	1	-0.0147	-0.0037

From a comparison of the results in the second section of Table II. with those in the first section, it appears that, under the conditions advocated by Rupp, the sulphite is not completely oxidised by the iodine. It seems that enough of the secondary action, by which the thiosulphate is oxidised beyond the condition of tetrathionate, takes place to counterbalance the error of incomplete oxidation when moderate amounts of sulphurous acid are handled, and more than enough for the smallest amounts, the secondary error predominating in such cases.

The results of experiments in which acid potassium carbonate was substituted for the acid sodium carbonate gave similar results.

So it appears that when Rupp's process gives results approximating the truth, it is due to the happy balancing of opposed errors. It seems quite possible that the same balancing of errors likewise occurs in the process for the determination of phosphorous acid described by Rupp and Fink (*Ber.*, 1902, xxxv., 3691).

In conclusion, I would like to thank Prof. F. A. Gooch for many kind suggestions.—*American Journal of Science*, 1905, xix., p. 237.

NOTICES OF BOOKS

Outlines of Inorganic Chemistry. By FRANK AUSTIN GOOCH and CLAUDE FREDERIC WALKER. New York: The Macmillan Company. London: Macmillan and Co., Ltd. 1905.

As a text-book for use in schools and colleges this book appears to be well above the average, especially when its very moderate price is taken into account. It is divided into two parts; in the first, and inductive part, dealing with the principles of chemistry, the development of modern theories is traced very logically, and if supplemented by a good course of practical work it should enable the student to acquire a thorough knowledge of chemical theory. One

of the chief merits of the book is the excellent balance preserved between detail and generalisation, so that neither is in the least degree sacrificed to the other. The second part of the book, which we should imagine would be read by the student side by side with the first, contains a systematic account of the elements and their chief compounds. The summaries of the most important properties and reactions of the various substances will be found of great use by examination candidates in co-ordinating their knowledge, as will also the paragraphs describing the characteristics of the natural groups. The book as a whole, although in some respects recalling the old familiar type of purely descriptive text book, crammed full of information, manages to maintain a decidedly higher level than these, and will be found worth keeping for reference even in a library containing far larger and more pretentious works.

Nieuwe Verhandelingen van het Bataafsch Genootschap der Proefondervindelijke Wijsbegeerte te Rotterdam. ("Recent Transactions of the Batavian Society of Experimental Science at Rotterdam"). Second Series. Vol. VI. Part I. Rotterdam: W. J. Van Hengel. 1905.

This volume of the "Transactions of the Batavian Scientific Society" contains two of the essays to which the gold medals of the Society have been awarded. The first of these papers, by Dr. C. W. Broers, contains a description of the author's experiments dealing with the duration of the virulence of tuberculous bacilli in milk, butter-milk, and butter respectively. Before attacking his subject the author appears to have carefully consulted all the necessary authorities, and to have arranged and performed his experiments with the utmost care. The second essay is entitled "An Inquiry into the Nature of the Sugar of some Vegetable Glucosides," and in it are described investigations of the action of emulsine upon various glucosides, such as arbutin, coniferin, aesculin, &c. Though the author does not appear to have arrived at any results which may be regarded as of great importance, the inquiry has obviously been well planned and carefully carried out.

Hypochlorite und Elektrische Bleiche. ("Hypochlorites and Electric Bleaches"). By Dr. EMIL ABEL. Halle-a-S.: Wilhelm Knapp. 1905.

THIS is a companion volume to an earlier one of the same series, by Viktor Engelhardt, which deals with the technical aspect of the subject, while Dr. Abel's work is occupied entirely with the theory of the preparation of bleaching liquors by electrochemical means, which really amounts to nothing more than the electrochemistry of solutions of the salts of hypochlorous acid. In considering this theory an unusually large number of factors has to be taken into account, and the thorough understanding of it necessitates the following of a fairly complicated explanation, which, however, Dr. Abel puts forward in as clear a manner as possible. He is always particularly careful to emphasise the difference between conclusions which have been proved experimentally on the one hand, and hypotheses and assumptions on the other, and he has incorporated in the volume the results of the most recent experiments, so that it forms a valuable and up-to-date guide to the preparation of bleaching liquors electrolytically.

Verflüssigtes Ammoniak als Lösungsmittel. ("Liquefied Ammonia as a Solvent"). By J. BRONN. Berlin: Julius Springer. 1905.

THE author of this monograph has endeavoured to give a complete account of all that is known of the use of liquid ammonia, and he hopes that he will thus awake additional interest in it as a solvent, and render reference to original publications dealing with its properties and applications superfluous. With this aim in view he has carefully collected all available information on the subject, and has

produced a most systematic review of the properties, both physical and chemical, of the liquid. He calls attention specially to its value from a technical point of view, and emphasises the fact that there is no serious difficulty in obtaining apparatus suitable for working with it, for it does not attack the heavy metals generally used for constructing apparatus, and at ordinary temperatures the pressure amounts to only 6 to 10 atmospheres.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 4, July 24, 1905.

Nature of the Hydrocyanic Glucoside obtained from Black Elder.—L. Quignard and J. Houdas.—The authors make an extract of the leaves of black elder. From the liquid obtained on the addition of semicarbazide a crystalline precipitate is formed. This semicarbazone is collected, dried, and re-crystallised from ether. Its analysis shows it to have the formula $\text{NH}_2\text{—CO—NH—N=CH—C}_6\text{H}_5$. When treated with HCl it decomposes, giving a liquid product boiling at 179° and having the characteristic smell of bitter almonds. These experiments therefore prove the leaves of black elder to contain amygdaline.

Catalytic Decomposition of Monochlor-formenic Derivatives in contact with Anhydrous Metallic Chlorides.—Paul Sabatier and A. Mailhé.—The authors find that the various anhydrous chlorides of the divalent metals (nickel, cobalt, iron, cadmium, lead, barium, &c.) act catalytically between the temperatures 260° and 300° on the primary monochlor-formenic derivatives, causing the latter to split up into hydrochloric acid and the corresponding ethylenic carbide. It is also evident that the secondary and tertiary derivatives, obtained by a single heating, undergo still more easily the same decomposition.

Fluorescence.—C. Camichel.—The experiments described in this paper prove that the intensity of the light emitted by fluorescence is proportional to the intensity of the exciting source of light. The author also verifies, by a new method, the already enunciated fact that the coefficient of absorption of a fluorescent body does not vary at the moment of fluorescence.

Influence of Water Vapour on the Reduction of Carbonic Anhydride by means of Carbon.—O. Boudouard.—The author performs a series of experiments to show the effect of the presence of water vapour on the reduction of carbon dioxide at temperatures between 650° and 1000° .

Synthesis of Zinc Silicates.—A. Duboin.—The zinc oxide is reacted upon by silica, the latter being dissolved in melted potassium fluoride. The products may be separated by means of the heavy solution of sodium iodide (a density of 3.46 being obtained). The first silicate has the formula $\text{K}_2\text{O}, 6\text{ZnO}, 4\text{SiO}_2$ and density 3.68. The second, formula $8\text{K}_2\text{O}, 9\text{ZnO}, 17\text{SiO}_2$ and density 2.96.

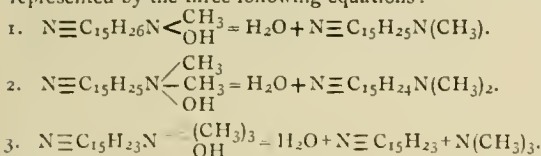
A Phosphorus Sub-iodide, and the Part Played by this Body in the Allotropic Transformation of Phosphorus.—R. Boulouch.—The author prepares a sub-iodide of phosphorus by the action of solar light on a mixture of iodine and phosphorus dissolved in very dry carbon disulphide. If the proportion of iodine is greater than would be present in the bi-iodide no effect is produced, but for less proportions of iodine a red precipitate is formed, which is produced more rapidly as the solution becomes more concentrated. This precipitate is collected and dried in a current of CO_2 at 100° , and its properties examined. To explain the catalytic action of this compound, at a high temperature (nearly 160°) the produc-

tion of bi-iodide of phosphorus is immediately followed by a reduction of this body by the white phosphorus. The iodide, PI_2 , becomes transformed into the sub-iodide in virtue of the necessarily exothermic reaction $7\text{P}(\text{white}) + \text{PI}_2 = 2\text{P}_4$; but, at 160° and above, the P_4I decomposes, forming once again the bi-iodide, more or less dissociated, $2\text{P}_4\text{I} = \text{PI}_2 + 7\text{P}(\text{red})$. This is also an exothermic reaction.

Potassium Iridio-chloro-nitrite.—L. Quennessen.—The author treats the double nitrite of iridium and potassium with dilute hydrochloric acid. This treatment is repeated several times; then the liquid evaporated, dried, and re-dissolved in water saturated with potassium chloride. A precipitate is given which, when purified, is seen to consist of little yellow crystals which act on polarised light. Analysis proves them to be of the composition $\text{Ir}_3\text{Cl}_{16}(\text{NO}_2)_8\text{K}_{12} \cdot 4\text{H}_2\text{O}$.

Action of Sodium Sulphite on Ethanal.—MM. Seyewetz and Bardin.—Sodium sulphite and ethanal, which have no action on each other in dilute solution, react violently when they are mixed in concentrated solution. The author investigates the best conditions for production of crotonic aldehyde by varying systematically the temperature of the reaction, the proportion of the reagents, the time of contact, and the concentration of the solutions.

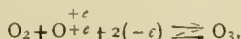
Sparteine: Hydrates of Methyl-, Dimethyl-, and Trimethyl-sparteinium.—Charles Moureu and Amand Valeur.—The authors investigate a series of reactions represented by the three following equations:—



Gentiane.—Georges Tanret.—Gentiane corresponds to the formula $\text{C}_{25}\text{H}_{28}\text{O}_{14}$. It is the first glucoside known which gives xylose amongst its products of decomposition. Its rarity has not yet enabled the author to thoroughly investigate the relations which exist between gentianine and gentiane.

Chemical Equilibrium of a System. Ammonia Gas and Primary Isoamylamine Chlorohydrate.—Félix Bidet.—Unsuitable for abstraction.

ERRATUM.—P. 63, col. 1. Instead of " $\text{O} + \text{O}_2$ " &c., the formula should read as follows:—



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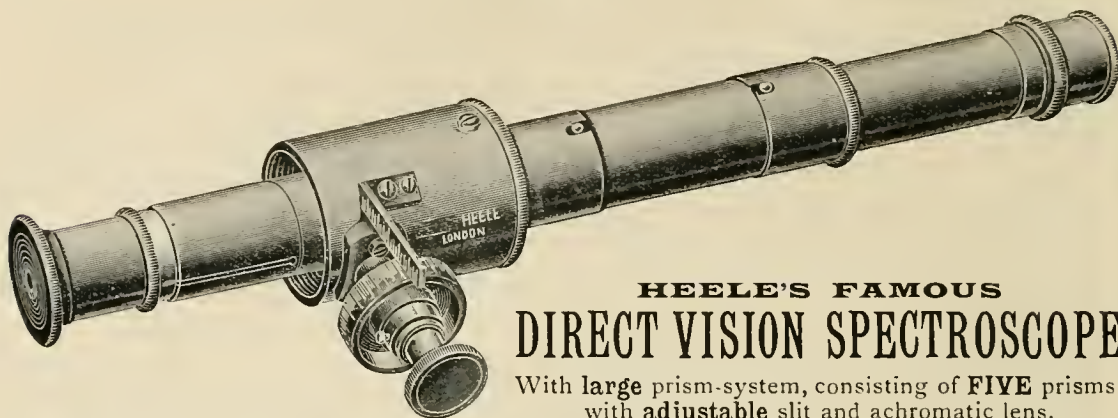
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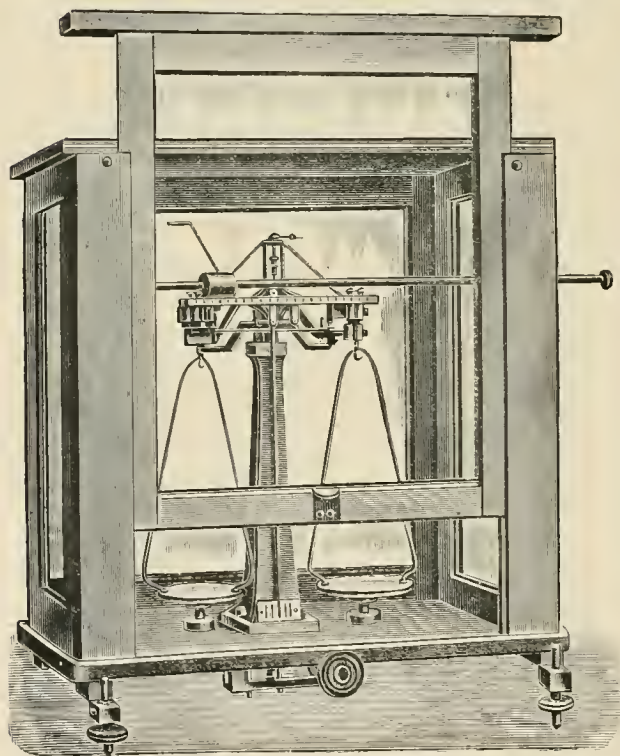
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VOL. XCII., No. 2388.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

SOUTH AFRICA, 1905.

SECOND PART OF ADDRESS OF THE PRESIDENT,

Prof. G. H. DARWIN, M.A., LL.D., Ph.D., F.R.S.

(Delivered at JOHANNESBURG, August 30th).

At Cape Town I attempted to make a general survey of evolution in its various branches, and laid down certain general propositions as to what seems common to all of them.

I then went on to consider how these general laws found an application in the most recent speculations as to the constitution of matter. The atoms of the elements and the molecules of chemical combinations are constructed on so minute a scale that it is no easy task to picture them to our minds. On the other hand, we see in the heavens arrangements of matter on a scale so vast that it is equally difficult to grasp. Both the inconceivably small and the inconceivably large should fall under a general law, if it is a true one; and the history of satellites, planets, and stars present at least as great an interest as that of atoms and molecules. Accordingly, the transition from the small to the large seemed to afford a convenient halting place in my Address, and I propose to-night to resume the discussion by considering various theories of celestial evolution. But I will first try to render the point of view intelligible which I desire to take. A short preliminary explanation for those who were not at Cape Town thus becomes necessary.

I desire to present the essential features which are common to evolution in all its branches, and this may be done most easily by reference to political institutions, because we all fancy we understand something of politics.

The complex interactions of man with man in a community are usually described by such comprehensive terms as "the State," "the Commonwealth," or "the Government." Various States differ widely in their constitution and in the degree of the complexity of their organisation, and we classify them by various general terms, such as "autocracy," "aristocracy," or "democracy," which express somewhat loosely their leading characteristics. But for the purpose of showing the analogy with physics we need terms of wider import than those habitually used in politics. All forms of the State imply inter-relationship in the actions of men, and action implies movement. Thus the State may be described as a configuration or arrangement of a community of men; or we may say that it implies a definite mode of motion of men—that is to say, an organised scheme of action of man on man. Political history gives an account of the gradual changes in such configurations or modes of motion of men as have possessed the quality of persistence or of stability to resist the disintegrating influence of surrounding circumstances.

In the history of a State we find this stability or power of persistence continually changing. It slowly rises to a maximum, and then declines; when it falls to nothing a revolution ensues, and a new form of government is established. This new mode of motion of men, or government, has at first but little stability, but it gradually acquires strength and permanence, until in its turn the slow decay in the power of persistence leads on to a new revolution. Such crises in political history may give rise to a condition in which the State is incapable of perpetuation

by transformation. This occurs when a savage tribe nearly exterminates another and leads the few survivors into slavery; the previous form of government then becomes extinct.

Now turn to the evolution of the various forms of life. The fundamental idea in the theory of Natural Selection is the persistence of those types of life which are adapted to their surrounding conditions, and the elimination by extermination of the ill-adapted types. The struggle for life amongst forms possessing various degrees of adaptation to slowly varying conditions is held to explain the transmutation of species. Although a different phraseology is used when we speak of the physical world, yet the idea is essentially the same. Theories of physical evolution involve the discovery of modes of motion or configurations of matter which are capable of persistence. The physicist describes such types as stable; the biologist calls them species.

The physicist, the biologist, and the historian alike watch the effect of slowly varying external conditions; they all observe the rise and decline of stability, with the consequent change of type of motion, transmutation of species, or revolution.

And now after this preface I turn to astronomical theories of evolution.

The German astronomer Bode long ago propounded a simple empirical law concerning the distances at which the several planets move about the sun, and his formula embraces so large a number of cases with accuracy that we are compelled to believe that it arises in some manner from the primitive conditions of the planetary system.

The explanation of the causes which have led to this simple law as to the planetary distances presents an interesting problem, and, although it is still unsolved, we may obtain some insight into its meaning by considering what may be called a working model of ideal simplicity.

Imagine, then, a sun round which there moves in a circle a single large planet. I will call this planet Jove, because it may be taken as a representative of our largest planet, Jupiter. Suppose next that a meteoric stone or small planet is projected in any perfectly arbitrary manner in the same plane in which Jove is moving; then we ask how this third body will move. It appears that under the combined attractions of the sun and Jove the meteoric stone will in general describe an orbit of extraordinary complexity, at one time moving slowly at a great distance from both the sun and Jove, at other times rushing close past one or other of them. As it grazes past Jove or the sun it may often but just escape a catastrophe, but a time will come at length when it runs it chances too fine and comes into actual collision. The individual career of the stone is then ended by absorption, and of course by far the greater chance is that it will find its Nirvana by absorption in the sun.

Next let us suppose that instead of one wandering meteoric stone or minor planet there are hundreds of them, moving initially in all conceivable directions. Since they are all supposed to be very small, their mutual attractions will be insignificant, and they will each move almost as though they were influenced only by the sun and Jove. Most of these stones will be absorbed by the sun, and the minority will collide with Jove.

When we inquire how long the career of a stone may be, we find that it depends on the direction and speed with which it is started, and that by proper adjustment the delay of the final catastrophe may be made as long as we please. Thus by making the delay indefinitely long we reach the conception of a meteoric stone which moves so as never to come into collision with either body.

There are, therefore, certain perpetual orbits in which a meteoric stone or minor planet may move for ever without collision. But when such an immortal career has been discovered for our minor planet, it still remains to discover whether the slightest possible departure from the prescribed orbit will become greater and greater, and ultimately lead to a collision with the sun or Jove, or whether the body will

travel so as to cross and re-cross the exact perpetual orbit, always remaining close to it. If the slightest departure inevitably increases as time goes on, the orbit is unstable; if, on the other hand, it only leads to a slight waviness in the path described, it is stable.

We thus arrive at another distinction; there are perpetual orbits, but some, and indeed most, are unstable, and these do not offer an immortal career for a meteoric stone; and there are other perpetual orbits which are stable or persistent. The unstable ones are those which succumb in the struggle for life, and the stable ones are the species adapted to their environment.

If, then, we are given a system of a sun and large planet together with a swarm of small bodies moving in all sorts of ways, the sun and planet will grow by accretion, gradually sweeping up the dust and rubbish of the system, and there will survive a number of small planets and satellites moving in certain definite paths. The final outcome will be an orderly planetary system in which the various orbits are arranged according to some definite law.

There is hardly room for doubt that if a complete solution for our solar system were attainable, we should find that the orbits of the existing planets and satellites are numbered amongst the stable perpetual orbits, and should thus obtain a rigorous mechanical explanation of Bode's law concerning the planetary distances.

In the first portion of my Address I described the orbits in which the corpuscles move in the atoms of matter, and drew attention to the resemblance to a planetary system. It may not, perhaps, be fanciful to imagine that some general mathematical method devised for solving a problem of cosmical evolution may find another application to miniature atomic systems, and may thus lead onward to vast developments of industrial mechanics. Science, however diverse its aims, is a whole, and men of science do well to impress on the captains of industry that they should not look askance on those branches of investigation which may seem for the moment far beyond any possibility of practical utility.

The theory which I have now explained points to the origin of the sun and planets from gradual accretions of meteoric stones, and it makes no claim to carry the story back behind the time when there was already a central condensation or sun about which there circled another condensation or planet. But more than a century ago an attempt had already been made to re-construct the history back to a yet remoter past, and, as we shall see, this attempt was based upon quite a different supposition as to the constitution of the primitive solar system. I myself believe that the theory I have just explained, as well as that to which I am coming, contains essential elements of truth, and that the apparent discordances will some day be reconciled. The theory of which I speak is the celebrated Nebular Hypothesis, first suggested by the German philosopher Kant, and later re-stated independently and in better form by the French mathematician Laplace.

Laplace traced the origin of the solar system to a nebula or cloud of rarefied gas congregated round a central condensation which was ultimately to form the sun. The whole was slowly rotating about an axis through its centre, and, under the combined influences of rotation and of the mutual attraction of the gas, it assumed a globular form, slightly flattened at the poles. The primeval globular nebula is undoubtedly a stable or persistent figure, and thus Laplace's hypothesis conforms to the general laws which I have attempted to lay down.

The nebula must have gradually cooled by radiation into space, and as it did so the gas must necessarily have lost some of its spring or elasticity, thus permitting a greater degree of condensation of the whole. The contraction led inevitably to two results: first, the central condensation became hotter; and, secondly, the speed of its rotation became faster. The accelerated rotation led to an increase in the amount of polar flattening, and the nebula at length assumed the form of a lens, or of a disk thicker in the middle than at the edges. Assuming the existence

of the primitive nebula, the hypothesis may be accepted thus far as practically certain.

From this point, however, doubt and difficulty enter into the argument. It is supposed that the nebula became so much flattened that it could not subsist as a continuous aggregation of gas, and a ring of matter detached itself from the equatorial regions. The central portions of the nebula, when relieved of the excrescence, resumed the more rounded shape formerly possessed by the whole. As the cooling continued, the central portion in its turn became excessively flattened through the influence of its increased rotation; another equatorial ring then detached itself, and the whole process was repeated as before. In this way the whole nebula was fissured into a number of rings surrounding the central condensation, whose temperature must by then have reached incandescence.

Each ring then aggregated itself round some nucleus which happened to exist in its circumference, and so formed a subordinate nebula. Passing through a series of transformations, like its parent, this nebula was finally replaced by a planet with attendant satellites.

The whole process forms a majestic picture of the history of our system. But the mechanical conditions of a rotating nebula are too complex to admit, as yet, of complete mathematical treatment; and thus, in discussing this theory, the physicist is compelled in great measure to adopt the qualitative methods of the biologist, rather than the quantitative ones which he would prefer.

Although the telescope seems to confirm the general correctness of Laplace's hypothesis, yet it is hardly too much to say that every stage in the supposed process presents to us some impossibility.

Thus, for example, the ring of Saturn seems to have suggested the theory to Laplace; but to take it as a model leads us straight to a quite fundamental difficulty. If a ring of matter ever concentrates under the influence of its mutual attraction, it can only do so round the centre of gravity of the whole ring. Therefore the matter forming an approximately uniform ring, if it concentrates at all, can only fall in on the parent planet and be re-absorbed. Some external force other than the mutual attraction of the matter forming the ring, and therefore not provided by the theory, seems necessary to effect the supposed concentration. The only way of avoiding this difficulty is to suppose the ring to be ill-balanced or lop-sided; in this case, provided the want of balance is pronounced enough, concentration will take place round a point inside the ring but outside the planet.

However, this is not the time to pursue these considerations further, yet enough has been said to show that the Nebular Hypothesis cannot be considered as a connected intelligible whole, however much of truth it may contain.

In the first theory which I sketched as to the origin of the sun and planets, we supposed them to grow by the accretions of meteoric wanderers in space, and this hypothesis is apparently in fundamental disagreement with the conception of Laplace, who watches the transformations of a continuous gaseous nebula. I must not pause to consider how these seemingly discordant views may be reconciled, but will merely say that I conceive both theories contain important elements of truth.

We have seen that, in order to explain the genesis of planets according to Laplace's theory, the rings must be ill-balanced or even broken. If the ring were so far from being complete as only to cover a small segment of the whole circumference, the true features of the occurrences in the births of planets and satellites might be better represented by conceiving the detached portion of matter to have been more or less globular from the first, rather than ring-shaped. Now this idea introduces us to another group of researches whereby mathematicians have sought to explain the birth of planets and satellites.

The solution of the problem of evolution involves the search for those persistent or stable forms which biologists would call species. The species of which I am now going

to speak may be grouped in a family, which comprises all those various forms which a mass of rotating liquid is capable of assuming under the conjoint influences of gravitation and rotation. If the earth were formed throughout of a liquid of the same density, it would be one of the species of this family; and indeed these researches date back to the time of Newton, who was the first to explain the figures of planets.

The ideal liquid planets we are to consider must be regarded as working models of actuality, and inasmuch as the liquid is supposed to be incompressible, the conditions depart somewhat widely from those of reality. Hence, when the problem has been solved, much uncertainty remains as to the extent to which our conclusions will be applicable to actual celestial bodies.

We begin, then, with a rotating liquid planet like the earth, which is the first stable species of our family. We next impart in imagination more rotation to this planet, and find by mathematical calculation that its power of resistance to any sort of disturbance is less than it was. In other words, its stability declines with increased rotation, and at length we reach a stage at which the stability just vanishes. At this point the shape is a transitional one, for it is the beginning of a new species with different characteristics from the first, and with a very feeble degree of stability or power of persistence. As a still further amount of rotation is imparted, the stability of the new species increases to a maximum and then declines until a new transitional shape is reached and a new species comes into existence. In this way we pass from species to species with an ever-increasing amount of rotation.

The first or planetary species has a circular equator like the earth; the second species has an oval equator, so that it is something like an egg spinning on its side on a table; in the third species we find that one of the two ends of the egg begins to swell, and that the swelling gradually becomes a well-marked protrusion or filament. Finally, the filamentous protrusion becomes bulbous at the end, and is only joined to the main mass of liquid by a gradually thinning neck. The neck at length breaks, and we are left with two separate masses which may be called planet and satellite.

In this ideal problem the successive transmutations of species are brought about by gradual additions to the amount of rotation with which the mass of liquid is endowed. It might seem as if this continuous addition to the amount of rotation were purely arbitrary, and could have no counterpart in Nature. But real bodies cool and contract in cooling, and I must ask you to believe that the effects of an apparently arbitrary increase of rotation may be produced by cooling.

The figures which I succeeded in drawing, by means of rigorous calculation, of the later stages of this course of evolution, are so curious as to remind one of some such phenomenon as the protrusion of a filament of protoplasm from a mass of living matter, and I suggest that we may see in this almost life-like process the counterpart of at least one form of the birth of double stars, planets, and satellites.

My Cambridge colleague Jeans has also made an interesting contribution to the subject by attacking the far more difficult case where the rotating fluid is a compressible gas. In this case also he finds a family of types, but the conception of compressibility introduced a new set of considerations in the transitions from species to species. The problem is, however, of such difficulty that he had to rest content with results which were rather qualitative than strictly quantitative.

It cannot be doubted that the supposed Laplacian sequence of events possesses a considerable element of truth, yet these latter schemes of transformation can be followed in closer detail. It seems, then, probable that both processes furnish us with crude models of reality, and that in some cases the first and in others the second is the better representative.

The moon's mass is one-eightieth of that of the earth,

whereas the mass of Titan, the largest satellite in the solar system, is $1/4600$ of that of Saturn. On the ground of this great difference between the relative magnitudes of all other satellites and of the moon, it is not unreasonable to suppose that the mode of separation of the moon from the earth may also have been widely different. The theory of which I shall have next to speak claims to trace the gradual departure of the moon from an original position not far removed from the present surface of the earth. If this view is correct, we may suppose that the detachment of the moon from the earth occurred as a single portion of matter, and not as a concentration of a Laplacian ring.

If a planet is covered with oceans of water and air, or if it is formed of plastic molten rock, tidal oscillations must be generated in its mobile parts by the attractions of its satellites and of the sun. Such movements must be subject to frictional resistance, and the planet's rotation will be slowly retarded by tidal friction in much the same way that a fly-wheel is gradually stopped by any external cause of friction. Since action and reaction are equal and opposite, the action of the satellites on the planet, which causes the tidal friction of which I speak, must correspond to a reaction of the planet on the motion of the satellites.

At any moment of time we may regard the system composed of the rotating planet with its attendant satellite as a stable species of motion, but the friction of the tides introduces forces which produce a continuous, although slow, transformation in the configuration. It is, then, clearly of interest to trace backwards in time the changes produced by such a continuously acting cause, and to determine the initial condition from which the system of planet and satellite must have been slowly degrading. We might also look forward, and discover whether the transformation tends.

Let us consider, then, the motion of the earth and moon revolving in company round the sun, on the supposition that the friction of the tides in the earth is the only effective cause of change. We are, in fact, to discuss a working model of the system, analogous to those of which I have so often spoken before; and it must suffice to set forth the result in its main outline as referring only to the past.

If we take the "day," regarding it as a period of variable length, to mean the time occupied by a single rotation of the earth on its axis, and the "month," likewise variable in absolute length, to mean the time occupied by the moon in a single revolution round the earth, the number of days in the month expresses the speed of the earth's rotation relatively to the speed of the moon's revolution.

Now in our retrospect both day and month are found continuously shortening; but as on the whole the month shortens much more quickly than the day, the number of days in the month also falls. We may, then, ask at once, What is the initial stage to which the gradual transformation points? I say, that on following the argument to its end the system may be traced back to a time when the day and month were identical in length, and were both only about four or five of our present hours. The identity of day and month means that the moon was always opposite to the same side of the earth; thus at the beginning the earth always presented the same face to the moon, just as the moon now always shows the same face to us. Moreover, when the month was only some four or five of our present hours in length, the moon must have been only a few thousand miles from the earth's surface—a great contrast with the present distance of 240,000 miles.

It might well be argued from this conclusion alone that the moon separated from the earth more or less as a single portion of matter at a time immediately antecedent to the initial stage to which she has been traced. But there exists a yet more weighty argument favourable to this view, for it appears that the initial stage is one in which the stability of the species of motion is tottering, so that the system presents the characteristic of a transitional form, which we have seen to denote a change of type or species in a previous case.

In discussing the transformations of a liquid planet we saw the tendency of the single mass to divide into two portions, and now we seem to reach a similar crisis from the opposite end, when in retrospect we trace back the system to two masses of unequal sizes in close proximity with one another. The argument almost carries conviction with it, but I have necessarily been compelled to pass over various doubtful points.

Time is wanting to consider other subjects worthy of notice which arise out of this problem, yet I wish to point out the fact that tidal friction is competent to explain the eccentricity of an orbit, because this conclusion has been applied in a manner to which I shall have occasion to return hereafter.

If, as has been argued, tidal friction has played so important a part in the history of the earth and moon, it might be expected that the like should be true of the other planets and satellites, and of the planets themselves in their relationship to the sun. But numerical examination of the several cases proves conclusively that this cannot have been the case. The relationship of the moon to the earth is in fact quite exceptional in the solar system, and we have still to rely on such theories as that of Laplace for the explanation of the main outlines of the solar system.

I have not yet mentioned the time occupied by the sequence of events sketched out in the various schemes of cosmogony, and the question of cosmical time is a thorny and controversial one.

Our ideas are absolutely blank as to the time requisite for the evolution either according to Laplace's nebular hypothesis, or the meteoritic theory. All we can assert is that they demand enormous intervals of time as estimated in years.

The theory of tidal friction stands alone amongst these evolutionary speculations in that we can establish an exact but merely relative time-scale for every stage of the process. Although it is true that the value in years of the unit of time remains unknown, yet it is possible to determine a period in years which must be shorter than that in which the whole history is comprised. If at every moment since the birth of the moon tidal friction had always been at work in such a way as to produce the greatest possible effect, then we should find that sixty million years would be consumed in this portion of evolutionary history. The true period must be much greater, and it does not seem unreasonable to suppose that 500 to 1000 million years may have elapsed since the birth of the moon. Such an estimate would not seem extravagant to geologists who have, in various ways, made exceedingly rough determinations of geological periods.

As far as my knowledge goes I should say that pure geology points to some period intermediate between 50 and 1000 millions of years, the upper limit being more doubtful than the lower. Thus far we do not find anything which renders the tidal theory of evolution untenable.

But the physicists have formed estimates in other ways which, until recently, seemed to demand in the most imperative manner a far lower scale of time. According to all theories of cosmogony, the sun is a star which became heated in the process of its condensation from a condition of wide dispersion. When a meteoric stone falls into the sun the arrest of its previous motion gives rise to heat, just as the blow of a horse's shoe on a stone makes a spark. The fall of countless meteoric stones, or the condensation of a rarefied gas, was supposed to be the sole cause of the sun's high temperature.

Since the mass of the sun is known, the total amount of the heat generated in it, in whatever mode it was formed, can be estimated with a considerable amount of precision. The heat received at the earth from the sun can also be measured with some accuracy, and hence it is a mere matter of calculation to determine how much heat the sun sends out in a year. The total heat which can have been generated in the sun divided by the annual output gives a quotient of about 20 millions. Hence it seemed to be im-

peratively necessary that the whole history of the solar system should be comprised within some 20 millions of years.

This argument, which is due to Helmholtz, appeared to be absolutely crushing, and for the last forty years the physicists have been accustomed to tell the geologists that they must moderate their claims. But for myself I have always believed that the geologists were more nearly correct than the physicists, notwithstanding the fact that appearances were so strongly against them.

And now, at length, relief has come to the strained relations between the two parties, for the recent marvellous discoveries in physics show that concentration of matter is not the only source from which the sun may draw its heat.

Radium is a substance which is perhaps millions of times more powerful than dynamite. Thus it is estimated that an ounce of radium would contain enough power to raise 10,000 tons a mile above the earth's surface. Another way of stating the same estimate is this:—The energy needed to tow a ship of 12,000 tons a distance of 6000 sea miles at 15 knots is contained in 22 ounces of radium. The *Saxon* probably burns five or six thousand tons of coal on a voyage of approximately the same length. Other lines of argument tend in the same direction.

Now we know that the earth contains radio-active materials, and it is safe to assume that it forms in some degree a sample of the materials of the solar system; hence it is almost certain that the sun is radio-active also.

This branch of science is as yet but in its infancy, but we already see how unsafe it is to dogmatise on the potentialities of matter. It appears, then, that the physical argument is not susceptible of a greater degree of certainty than that of the geologists, and the scale of geological time remains in great measure unknown.

I have now ended my discussion of the solar system, and must pass on to the wider fields of the stellar universe.

Only a few thousand stars are visible with the unaided eye, but photography has revealed an inconceivably vast multitude of stars and nebulae, and every improvement in that art seems to disclose yet more and more. It seems useless to consider whether the number of stars has any limit, for infinite number, space, and time transcend our powers of comprehension. We must then make a virtue of necessity, and confine our attention to such more limited views as seem within our powers.

A celestial photograph looks at first like a dark sheet of paper splashed with whitewash, but further examination shows that there is method in the arrangement of the white spots. Thus there is order of some sort in the heavens, and, although no reason can be assigned for the observed arrangement in any particular case, yet it is possible to obtain general ideas as to the succession of events in stellar evolution.

Besides the stars there are numerous streaks, wisps, and agglomerations of nebulosity, whose light we know to emanate from gas. Spots of intenser light are observed in less brilliant regions; clusters of stars are sometimes imbedded in nebulosity, while in other cases each individual star of a cluster stands out clear by itself. These and other observations force on us the conviction that the wispy clouds represent the earliest stage of development, the more condensed nebulae a later stage, and the stars themselves the last stage. This view is in agreement with the nebular hypothesis of Laplace, and we may fairly conjecture that chains and lines of stars represent pre-existing streaks of nebulosity.

Change is obviously in progress everywhere, as well in each individual nebula and star as in the positions of these bodies relatively to one another. But we are unable even to form conjectures as to the tendency of the evolution which is going on. This being so, we cannot expect, by considering the distribution of stars and nebulae, to find

many illustrations of the general laws of evolution which I have attempted to explain; accordingly, I must confine myself to the few cases where we at least fancy ourselves able to form ideas as to the stages by which the present conditions have been reached.

Up to a few years ago there was no evidence that the law of gravitation extended to the stars, and even now there is nothing to prove the transmission of gravity from star to star. But in the neighbourhood of many stars the existence of gravity is now as clearly demonstrated as within the solar system itself. The telescope has disclosed the double character of a large number of stars, and the relative motion of the pairs of companions has been observed with the same assiduity as that of the planets. When the relative orbit of a pair of binary or double stars is examined, it is found that the motion conforms exactly to those laws of Kepler which prove that the planets circle round the sun under the action of solar gravitation. A leading characteristic of all these double stars is that the two companions do not differ enormously in mass from one another. In this respect these systems present a strongly marked contrast with that of the sun, attended as it is by relatively insignificant planets.

In the earlier part of my Address I showed how theory indicates that a rotating fluid body will as it cools separate into two detached masses. Mathematicians have not yet been able to carry their analysis far enough to determine the relative magnitudes of the two parts, but as far as we can see the results point to the birth of a satellite whose mass is a considerable fraction of that of its parent. Accordingly, See (who devotes his attention largely to the astronomy of double stars), Alexander Roberts, and others consider that what they have observed in the heavens is in agreement with the indications of theory. It thus appears that there is reason to hold that double stars have been generated by the division of primitive and more diffused single stars.

But if this theory is correct we should expect the orbit of a double star to be approximately circular; yet this is so far from being the case that the eccentricity of the orbits of many double stars exceeds by far any of the eccentricities in the solar system. Now, See has pointed out that when two bodies of not very unequal masses revolve round one another in close proximity, the conditions are such as to make tidal friction as efficient as possible in transforming the orbit. Hence we seem to see in tidal friction a cause which may have sufficed not only to separate the two component stars from one another, but also to render the orbit eccentric.

I have thought it best to deal very briefly with stellar astronomy in spite of the importance of the subject, because the direction of the changes in progress is in general too vague to admit of the formation of profitable theories.

We have seen that it is possible to trace the solar system back to a primitive nebula with some degree of confidence, and that there is reason to believe that the stars in general have originated in the same manner. But such primitive nebulae stand in as much need of explanation as their stellar offsprings. Thus, even if we grant the exact truth of these theories, the advance towards an explanation of the universe remains miserably slight. Man is but a microscopic being relatively to astronomical space, and he lives on a puny planet circling round a star of inferior rank. Does it not, then, seem as futile to imagine that he can discover the origin and tendency of the universe as to expect a housefly to instruct us as to the theory of the motions of the planets? And yet, so long as he shall last, he will pursue his search, and will no doubt discover many wonderful things which are still hidden. We may, indeed, be amazed at all that man has been able to find out, but the immeasurable magnitude of the undiscovered will throughout all time remain to humble his pride. Our children's children will still be gazing and marvelling at the starry heavens, but the riddle will never be read.

ON THE

REFRACTIVE INDEX OF GASEOUS FLUORINE.*

By C. CUTIIBERTSON and E. B. R. PRIDEAUX, M.A., B.Sc.

THE authors have determined the refractive index of gaseous fluorine for sodium light by means of Jamia's refractometer. Five experiments gave values for the refractivity $(\mu - 1)10^6$ of 195, 177, 192, 194, and 198. The discrepancy exhibited by the second experiment can be accounted for, and it is believed that the mean of the other four experiments, 195, is within 2 or 3 per cent of the true value.

The gas was prepared in a copper electrolytic tube, similar to that used by M. Moissan, and, after being purified from the vapour of hydrofluoric acid and from ozone, was made to displace dry air from a refractometer tube of platinum-iridium, whose ends were closed by plates of fluorspar. It was found by experience that it was impossible to obtain the gas completely free from air, or oxygen produced during electrolysis, and it was necessary, therefore, to analyse the mixture of gases contained in the refractometer tube at the moment when the index was observed.

The method employed for this purpose was to bring the gases into contact with dry lead filings in a closed space, and to estimate the volume of fluorine from the contraction. When the refractometer tube was filled with the gases produced by electrolysis it was disconnected from the source of supply, and its exit and entry tubes rapidly connected with two closed burettes, half filled with mercury, having at their upper extremities a narrow tube containing a large quantity of dry lead filings. Each closed burette was in communication with an open tube, and one was also connected with a reservoir of mercury. The open tubes were connected by a wire passing over a pulley, so that, when one was raised the other fell by an equal height. By moving these tubes the mixture of gases in the refractometer tube was pushed into the tube containing the lead filings, where the fluorine was absorbed as lead fluoride. As contraction occurred the pressure was equalised by letting in mercury from the reservoir, and in this manner the quantity of fluorine present was measured. The oxygen contained in the residual gases was measured by burning with phosphorus, and the remainder was found to be nitrogen.

Throughout the experiments it was observed that the amount of oxygen present in the current of gases proceeding from the electrolytic tube was always in excess of that due to the air present. After prolonged investigation it was ascertained that this oxygen was not formed by the action of fluorine on moisture in the train of purifiers, but was produced by electrolysis, probably from water absorbed by the solution. Contrary to expectation, this water was not electrolysed away before the fluorine appeared, but persisted throughout the experiment, perhaps owing to the gradual melting of a crystalline solid in the electrolytic tube.

In a recent paper (*Phil. Trans.*, 1905, A, vol. cciv., p. 323), one of the authors has attempted to show that the refractivities of the different members of the same chemical group are related in the ratios of small integers; and it was observed that, if this coincidence were not due to chance, the refractivity of fluorine should bear to that of chlorine the ratio of 1 to 4, which those of neon, oxygen, and nitrogen bear to argon, sulphur, and phosphorus respectively. This prediction has been verified. The refractivity of chlorine for sodium light is 768, or 192×4 ; and that now found for fluorine is 195, a discrepancy of $1\frac{1}{2}$ per cent, which is well within the limits of error of the experiment.

Chemical Oxydases.—G. Baudran.—The author has investigated the action of chlorine, bromine, and iodine on the alkaloids and the toxins.—*Comptes Rendus*, cxli., No. 5.

* Abstract of a Paper read before the Royal Society, June 8, 1905.

THE ABSORPTION SPECTRUM
AND FLUORESCENCE OF MERCURY VAPOUR.*

By W. N. HARTLEY, D.Sc., F.R.S.

HAVING undertaken the investigation of the absorption spectra of metals in a state of vapour, the first substance examined was mercury, and as the results are interesting I have deemed it advisable to make them a separate communication to the Society. F. P. le Roux describes the vapour of mercury as having a bluish colour (*Comptes Rendus*, 1860, vol. li., p. 171), and according to R. J. Strutt, it transmits a feeble steel-blue colour, but the absorption coefficient is small (*Phil. Mag.*, 1902, [6, vol. iv., p. 596; and 1903, vol. vi., p. 76]).

Experimental.—The substance to be volatilised was contained in a flask of Heraeus' quartz-glass, with a side tube to the neck from which the metal may be distilled and condensed. To the side tube a water-jacket is fitted, through which a constant stream of water may be passed if necessary. The rays from the condensed spark of a pair of lead-cadmium and tin-cadmium electrodes were passed through the flask and on to a cylindrical condensing lens of quartz which focussed the rays on to the slit of a quartz spectrograph.

The mercury to be used was first purified by distillation. The photographic plates used were various, such as "Rainbow Fast," Warwick plates, Lumière isochromatic, yellow-green sensitive, and Cadett and Neall's "Lightning Spectrum" plates. The mercury vapour in the flask was at a pressure of 8.47 m.m., the barometer standing at 763 m.m., but the vapour was under a pressure of a column of 8.4 m.m. of mercury above that of the atmosphere. The temperature was about 360° C., the boiling-point at 760 m.m. being 357°. The volume of the vapour was 31 c.c., and its weight was calculated to be 0.133 grm. The thickness of the layer of vapour was 37 m.m.

Several photographs were taken and particular care was exercised so as to have both ends of the spectrum as well as the central part in accurate focus. The developer used was "imogen sulphite."

The Absorption Spectrum.—The whole rays were transmitted from the red to a point in the ultra-violet where there is a tin-line at λ 2571.67. From there to λ 2526.8 there is a very sharply defined and intense absorption band, somewhat degraded on the side towards the red, beyond that the rays are transmitted with full intensity to a wavelength about 2000.

The Fluorescence.—When the mercury was boiling briskly the whole side of the flask nearest to the spark was lighted up with a green fluorescence; this penetrated about one-third of the space within the flask, and lighted up the interior. The quartz-glass itself was not fluorescent in the slightest degree.

When all the liquid mercury had become converted into vapour, the temperature no doubt rose above that of the boiling mercury, the vapour was quiescent, and the fluorescence ceased. The interior of the flask was then quite dark. By shaking some of the condensed cold mercury down into the flask, the fluorescence was resumed directly the liquid boiled again, but the dropping of cold mercury into the heated vapour caused condensation, and only after the flask had again become filled with the mercury vapour was the fluorescence fully displayed.

When the vapour was rising from the boiling globule of mercury after the cold metal had condensed all within the flask, the vapour could be seen by its fluorescence to undergo condensation in the upper part of the vessel and descend to the hotter space below.

It occurred to me that the actual fluorescence might be associated with oxidation of the vapour, and that it appeared only when such chemical action was taking place, but subsequent observations showed that this could not be the case, because the temperature was above that when

oxidation could occur at the time when the fluorescence was most brilliant, and when it most completely filled the vessel, and also when the mercury vapour had expelled all the air. When the temperature rose above the boiling-point of mercury and excess of liquid mercury and vapour had been expelled from the flask, the fluorescence ceased.

This fact leads to the inference that the fluorescence occurs only between a lower and a higher limit of temperature. What these small differences really are I had no means of determining. Having established the fact that the property of selective absorption is possessed by small quantities of mercury vapour, it was resolved to ascertain whether the band showed itself in solutions of mercury compounds. As a rule the absorption spectra of compounds differ from those of the elements entering into their composition entirely, as in the case of the halogen compounds of the alkali metals; sometimes it is a question of degree, as in the case of the compounds of the rare earth metals, in which similar bands are observed in different salts of the same metal, but in different positions, which vary with the molecular weight of the salts; and there are, still further, other instances where the absorption bands of the solutions are distinctly the properties of the salts, as in the case of the chlorides, bromides, and iodides of cobalt. The salt chosen for examination, because it is the most definite and most soluble, was mercuric chloride. It was examined in cells of 40 m.m. thick, diminishing to 1 m.m. in thickness. The solution contained in the same volume ten times as much mercury as the vapour which filled the flask, or 1.8 grms. of mercuric chloride in 31 c.c. of water; more dilute solutions were examined containing 0.18 grm. and 0.018 grm. No absorption band was visible on any of the spectra photographed, but there was a continuous absorption at the more refrangible end of the spectrum which regularly diminished as the quantity of mercuric chloride in the solution decreased.

Further details are as follows:—

1.8 grms. of mercuric chloride in a cell 40 m.m. thick transmitted all rays to λ 2702, in 1 m.m. to λ 2572; 0.18 grm. in a cell 2 m.m. thick, transmitted all rays to λ 2265; and 0.018 grm. in similar circumstances transmitted very feebly to λ 2145.

The absorption band in the vapour of mercury belongs to the vapour and is accompanied by strong fluorescence between a certain maximum and minimum of temperature lying very near to the boiling-point.

In studying the fluorescence of solutions of organic compounds I have shown that it is necessary to use the ultra-violet rays and quartz apparatus, as it was found that fluorescence was associated very generally with a powerful absorption of rays in the ultra-violet ("Observations on the Origin of Colour and Fluorescence," *Chem. Soc. Trans.*, 1893, vol. lxiii., p. 245—256). It is a question still undecided whether the rays absorbed by mercury vapour as shown by the band I have measured, reappear with a lowered refrangibility as yellowish green light in accordance with the law of Stokes.

The spectra were photographed with all due care by my assistant, Mr. Douglas Mellon, A.R.C.Sc.I.

THE PRECIPITATION OF BARIUM BROMIDE
BY HYDROBROMIC ACID.

By NORMAN C. THORNE.

In former articles from the Kent Chemical Laboratory of Yale University, processes for the separation and determination of certain chlorides, hydrous or anhydrous, by the action of hydrochloric acid have been studied (*Mar. Am. Journ. Sci.*, [3], xliii., 521; Gooch and Havens, *Ibid.*, [4], ii., 416; Havens, *Ibid.*, [4], iv., 111; [4], vi., 45 and 396). The present article deals with the similar separation and determination of barium bromide by the agency of hydrobromic acid.

* A Paper communicated to the Royal Society.

The hydrobromic acid used in the experiments to be described was prepared by dropping from a stoppered funnel liquid bromine into naphthalene dissolved in kerosene, passing the hydrogen evolved through a purifying tower charged in layers with glass-wool and red phosphorus and a water trap, and saturating distilled water with the gas thus purified.

Pure barium bromide was made by dissolving barium chloride in water, precipitating barium carbonate by ammonium carbonate and ammonium hydroxide, washing the precipitate by decantation, and dissolving it in hydrobromic acid. This solution of barium bromide was evaporated to dryness, and the barium bromide thus obtained was used in the following experiments.

In the first series of experiments a weighed amount of the barium bromide was dissolved in the least volume of water, and treated with hydrobromic acid or with a mixture of hydrobromic acid and ether in equal volumes. The liquid was saturated with hydrobromic acid gas, and filtered upon asbestos, and the precipitate washed by a mixture of hydrobromic acid and ether, dried in air-bath or over Bunsen flame, and weighed as BaBr₂. The details of these experiments are given in Table I.

TABLE I.

BaBr ₂ taken.	HBr.	HBr and ether.	BaBr ₂ found.	Error.
Grm.	C.c.	C.c.	Grm.	Grm.
0.2932	30	—	0.2934	+0.0002
0.1264	30	—	0.1260	-0.0004
0.1134	30	—	0.1132	-0.0002
0.1347	—	30	0.1367	+0.0020
0.1040	—	30	0.1035	-0.0005
0.0744	—	20	0.0748	+0.0004
0.1197	—	30	0.1211	+0.0014
0.4327	30	—	0.4345	+0.0018

Considerable difficulty was had in drying the barium bromide so as to obtain a constant weight, and the barium bromide prepared in the manner described did not dissolve completely. The results of these experiments are thereby lacking in uniformity. Presuming that the source of inaccuracy is to be looked for in the formation of an oxybromide, the precipitate in the next experiments, after filtering upon asbestos, was treated with ammonium bromide and then dried over a radiator, at first at a low temperature and finally at a temperature high enough to drive off the ammonium bromide. When the thermometer inside of the radiator showed a temperature of 250° C., all the ammonium bromide disappeared and left a barium bromide which gave constant results, as shown in Table II.

TABLE II.

BaBr ₂ taken.	HBr and ether.	BaBr ₂ found.	Error.
Grm.	C.c.	Grm.	Grm.
0.1330	30	0.1534	+0.0004
0.1013	30	0.1016	+0.0003
0.2769	30	0.2760	-0.0009
0.2359	30	0.2353	-0.0006
0.1580	30	0.1579	-0.0001
0.2955	30	0.2947	-0.0008
0.2822	30	0.2813	-0.0009
0.1962	30	0.1962	0.0000
0.4127	30	0.4125	-0.0002
0.2751	30	0.2750	-0.0001
0.3181	30	0.3183	+0.0002
0.3049	30	0.3039	-0.0010
0.3754	30	0.3752	-0.0002

These results indicate plainly that barium bromide, prepared in a state of purity and free from oxybromide, may be completely precipitated from solution in water by treatment with a mixture of hydrobromic acid and ether in equal parts and saturation of the liquid with hydrogen bromide.

Some experiments in which precipitation was effected by a mixture of concentrated hydrobromic acid and ether in

equal parts, without saturating with the gas, led to similar results. In these experiments the material weighed out was the crystallised hydrous barium bromide, BaBr₂·2H₂O.

TABLE III.

BaBr ₂ ·2H ₂ O taken.	HBr+ether (1:1).	BaBr ₂ found.	BaBr ₂ calculated.	Error.
Grm.	C.c.	Grm.	Grm.	Grm.
0.2008	30	0.1793	0.1790	+0.0003
0.2041	30	0.1822	0.1820	+0.0002
0.2047	30	0.1821	0.1825	-0.0004
0.2171	30	0.1937	0.1936	+0.0001
0.3101	30	0.2768	0.2765	+0.0003
0.5035	30	0.4496	0.4490	+0.0006
0.5015	30	0.4476	0.4473	+0.0003

The action of hydrobromic acid upon barium chloride was next studied, with or without the presence of salts of calcium and magnesium.

A weighed amount of barium chloride, BaCl₂·2H₂O, was dissolved in the least volume of water and treated with a mixture of hydrobromic acid and ether in equal volume. The whole solution was saturated with hydrobromic acid gas, filtered upon asbestos, and then, to make sure that no barium oxybromides might be formed, treated with ammonium bromide, dried, and weighed as BaBr₂.

TABLE IV.

BaCl ₂ ·2H ₂ O taken.	CaCO ₃ .	MgCO ₃ .	HBr + ether (1:1).	BaBr ₂ found.	Theory as BaBr ₂ .	Error in BaBr ₂ .
Grm.	Grm.	Grm.	C.c.	Grm.	Grm.	Grm.
0.2253	—	—	30	0.2744	0.2741	+0.0003
0.2088	—	—	30	0.2538	0.2540	-0.0002
0.3273	—	—	30	0.3975	0.3982	-0.0007
0.3177	—	—	30	0.3864	0.3865	-0.0001
0.5041	0.5000	—	30	0.6134	0.6143	-0.0009
0.5083	0.5000	—	30	0.6185	0.6191	-0.0006
0.5046	0.5000	—	30	0.6139	0.6136	+0.0003
0.5022	0.5000	—	30	0.6110	0.6104	+0.0006
0.5018	0.5000	—	30	0.6106	0.6108	-0.0002
0.5007	—	0.3000	30	0.6087	0.6092	-0.0005
0.5048	—	0.3000	30	0.6144	0.6142	+0.0002

From these results it is obvious that barium may be separated and determined as the bromide in presence of salts of calcium and magnesium; and it appears also that when the proportion of hydrobromic acid to the barium chloride is that of the experiment and the precipitate ignited with ammonium bromide, the results are in practical accord with those which should be obtained if the precipitate consists entirely of barium bromide.

On the other hand, it appears from the series of experiments given in Table V. that when a sufficiency of hydrochloric acid is added to the water solution of barium bromide, the precipitate falls practically as the chloride.

TABLE V.

BaBr ₂ ·2H ₂ O taken.	HCl used.	Ether.	BaCl ₂ found.	BaCl ₂ theory.	Error in BaCl ₂ .
Grm.	C.c.	C.c.	Grm.	Grm.	Grm.
0.2044	25	5	0.1279	0.1277	+0.0002
0.2011	25	5	0.1258	0.1257	+0.0001
0.5021	25	5	0.3138	0.3138	0.0000
0.5037	50	10	0.3148	0.3147	+0.0001
0.5020	25	5	0.3135	0.3137	-0.0002
0.3868	25	5	0.2418	0.2417	+0.0001

So it appears that precipitation is complete in presence of a sufficiency of either acid, and that the precipitate will fall chiefly as the bromide or as the chloride, according to the proportions of hydrobromic acid and hydrochloric acid present.

It was thought a matter of interest in this connection to test the constitution of the precipitates when incomplete precipitation is brought about by addition of one of these acids, the other being present in considerable proportion,

though in amount wholly insufficient to produce by itself precipitation in the volume of water used for solution of the barium salts.

Table VI. is the record of experiments in which 1 grm. of barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, was dissolved in water, hydrochloric acid added to incipient precipitation, and then an amount of hydrobromic acid which by itself would produce no precipitation in the water solution. The precipitate was dried and weighed, and the content in bromine determined by the method of Baubigny and Rivals (*Comptes Rendus*, cxxv., 527, 607).

TABLE VI.

$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ taken. Grm.	Water for solution. C.c.	HBr added. C.c.	HCl added. C.c.	Pre- cipitate. Grm.	Bromine in pre- cipitate. Grm.	BaBr_2 in precipi- tate. Grm.
I	30	3	22	0.5037*	0.0129	0.0240
I	42	5	31	0.6241†	0.0141	0.0263
I	40	5	30	0.6338†	0.0202	0.0375

* Dried three months in desiccator over sulphuric acid.

† Dried six hours at 80° and twelve hours in desiccator over sulphuric acid.

The meaning of these results seems to be that the precipitation of the bromide is induced by the action of the hydrogen chloride upon the solvent, water. The production of free bromine ions and barium ions to the amount of the solubility product of barium bromide in water is, under the conditions, an impossibility. It this be admitted, it seems highly probable that precipitation of barium chloride is likewise conditioned by the action of the hydrogen chloride upon the solvent.

It has been customary on the part of some to explain the similar precipitation of other chlorides soluble in water, like sodium chloride, by large amounts of hydrochloric acid, upon the assumption that insolubility is due to increased concentration of the chlorine ions, and such processes have been held to be typical of processes in which precipitation is affected by concentration of the free ions. It seems more probable, however, that it is the action of the hydrogen chloride upon the solvent which is the effective thing in such precipitations, as in the precipitation of barium bromide, after addition of hydrochloric acid, by an amount of hydrobromic acid wholly insufficient to cause precipitation in the water solution.

I wish to express my thanks to Prof. Gooch for suggestions and advice given during the progress of this work.—*American Journal of Science*, xviii., p. 441.

NOTICES OF BOOKS.

A Class-book of Elementary Chemistry. By W. W. FISHER, M.A., F.C.S. Fifth Edition, Revised and Enlarged. Oxford: Clarendon Press. 1905.

NUMEROUS important additions have been made to this class-book, which appears to contain a good grounding for the student of elementary chemistry. The plan of the first edition is followed, but the matter has been carefully brought up to date, in accordance with our latest knowledge of the developments of the science. A new feature is the addition of several chapters on organic chemistry. In these the properties and methods of preparation of various typical compounds—such as alcohol, oxalic acid, toluene—are described, and simple constitutional and structural formulæ are also discussed. The space devoted to organic chemistry is only a very small part of the whole, with the result that the treatment is rather too sketchy to be of any real use to the student, but in other respects the book appears to be a very fair specimen of the descriptive class of books on elementary chemistry.

Dispensing Made Easy. By WM. G. SUTHERLAND, M.B. (Aberd.). Second Edition. Bristol: John Wright and Co. London: Simpkin, Marshall, Hamilton, Kent, and Co., Ltd. 1905.

THIS little book well deserves the favourable reception accorded to it, and we are not surprised to learn that it has already run through its first edition. The second edition has been made rather fuller than the first in the way of additional formulæ, thoroughly tested by experience, and has been revised, so that it provides a most handy and reliable practical guide from which both the dispenser and the medical man can glean much useful information. The book contains, in a very concise form, a great variety of formulæ, practical hints on dispensing (specially with a view to ensuring the utmost economy both of money and time), and also ample space for memoranda and private formulæ.

Twenty-eighth Annual Report of the Connecticut Agricultural Experiment Station. For the Year ending October 31, 1904. New Haven, Conn.: The Tuttle, Morehouse, and Taylor Company. 1905.

A LARGE amount of useful matter is contained in this report, which gives a full account of the valuable work done by the Connecticut Agricultural Station. The report is sent free to any citizen of the State who applies for it, and, under certain circumstances, free analyses of fertilisers, foods, &c., are made for the benefit of the citizens. The report contains very valuable information concerning the price, composition, and actual value of large numbers of manures and commercial feeding-stuffs, the results in the case of the latter having been already published as a Bulletin in January of this year. The standards of purity for food products adopted by the Station are given at length, and the results of the analyses of some hundreds of substances of all kinds are tabulated. As the dealer and brand are in all cases stated in full, the citizen of Connecticut may very readily avoid purchasing adulterated or inferior foods of any description. Moreover, the analytical chemist will find in the book some useful hints as to methods of analysis, which experience has shown are the most convenient and accurate. Besides these chemical reports, the book includes the State Entomologist's Bulletin, containing notes on the identification and destruction of injurious insects, and also the results so far obtained during the mosquito investigation; and the State Botanist describes his researches on various blights; these two sections being copiously illustrated by plates.

Buletinul Societatii de Stiinte din Bucuresti, Romania. ("Bulletin of the Scientific Society of Bucharest, Roumania"). Vol. XIV. Bucuresti: Imprimeria Statului. 1905.

THIS volume contains the minutes of two meetings of the flourishing Scientific Society of Bucharest, as well as several papers—some of which are written in French—on mathematical, biological, and other subjects. One communication only deals with a chemical subject, namely, a paper by Dr. Adriano Ostrogovich on methyl diamino-triazine, which contains a very complete account of the thorough investigation of the properties and reactions of the triazine and its chief derivatives.

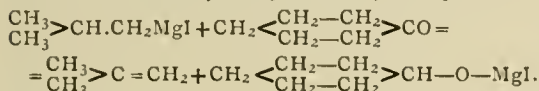
Simple Method of Preparing Halogen Alkyls.—R. F. Weinland and Karl Schmid.—Neutral esters of sulphuric acid are formed by the action of silver sulphate upon alkyl halogens. The reverse reaction, i.e., the formation of alkyl haloids from the dialkyl sulphate and metallic haloid, takes place readily in aqueous solution as follows:— $\text{SO}_2(\text{CH}_3)_2 + \text{KI} = \text{CH}_3\text{I} + \text{SO}_4\text{K}(\text{CH}_3)$. This method is very simple, and the alkyl halogens are obtained by it in the pure state, the yield being almost quantitative. Various methyl haloids may be prepared by this method, and also the ethyl compounds, but in the case of the latter the reaction takes place more slowly.—*Ber.*, xxxviii., No. 10.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 5, July 31, 1905.

A Secondary Reaction of Halogen Organo-magnesium Compounds.—Paul Sabatier and A. Mailhe.—The authors observe certain secondary reactions taking place when the aromatic or cyclo-forminic acetones react on various organo-magnesium halogen compounds. In the case of isobutyl and its derivatives this reaction is most marked, and may be represented by the equation—

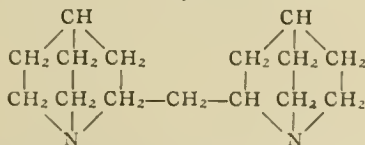


This reaction is reduced to a minimum when the temperature is very low.

State of Matter when nearing its Critical-point.—Gabriel Bertrand and Jean Lecarme.—The author's experiments show that when nearing the critical-point, and also at a temperature rather higher than this point, matter can exist at the same time in a liquid and gaseous state. In the case of a single substance there is present in the tube, not only a layer of pure liquid and a layer of pure vapour, but a layer of solution of vapour in liquid and a solution of liquid in vapour. This latter is doubtless relatively less concentrated than the former. The solubility of the vapour in the liquid, and the dissolving power of this vapour for the liquid, increases with the temperature and pressure. When the critical temperature is reached, the density of the two layers becomes identical. But it is quite perceptible that, at a decidedly higher temperature, a portion of the matter may still retain its liquid state.

Different Stages of Oxidation of Aluminium Powder.—M. Kohn-Abreast.—When aluminium powder is heated in a boat in contact with air to accurately measured temperatures and for accurately determined periods of time, the author finds that the quantities of oxygen taken up by the powder vary according to the method of operation. The velocity of the current of air exercises a most marked influence on appearance of the metal and on the magnitude of the oxidation.

Constitution of Spartein.—Charles Moureu and Amand Valeur.—The authors make a series of experiments to discover the constitution of spartein, and find it to be represented by the following formula, in which each atom of nitrogen is united to an asymmetric carbon:—



This formula, recognised by the presence of two bicyclic nitrogen radicals in symmetric position, agrees perfectly with the facts revealed by the researches of MM. Willstätter and Marx and MM. Herzog and Meyer.

Variations of the Basic Function in Chromium Salts.—Albert Colson.—In order to explain the inactivity of a normally prepared chromic pentasulphate, the author had to admit that the green oxide precipitated from chrome alum is a condensed oxide due to loss of water, $2\text{Cr}(\text{OH})_3 = \text{H}_2\text{O} + \text{O} \cdot \text{Cr}_2(\text{OH})_4$. If this is the case, a weak monobasic acid should give with this base a derivative of the form $\text{O} \cdot \text{Cr}_2\text{N}_3$, and not the sesqui-salt Cr_2N_6 . This is what happens in reality when 1 mol. of this oxide is left to

digest with 6 mols. of dilute cold acetic acid. A violet solution is obtained, having the appearance of a normal acetate, but which in reality contains one-third part of acetic acid in the free state. The author proves this fact by several experiments.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxviii., No. 10, 1905.

Crystalline Form of Sodium Formaldehyde Sulphoxylic Acid (Rongalite C).—A. Osann.—This salt, the first derivative of a new acid H_2SO_2 , corresponding to an oxide SO , is employed in calico printing. The constitutional formula is probably $\text{CH}_2 < \begin{array}{c} \text{OH} \\ \text{O} \cdot \text{SO} \cdot \text{H} \end{array}$. The sodium salt is characterised by a remarkable power of crystallisation. Perfectly formed crystals, weighing 400 grms. may be obtained without difficulty, but unfortunately the substance is strongly hygroscopic, so that the measurements of the crystals are affected by the moistness of their surfaces. The substance is very soluble in water, 1 litre of cold water dissolving 500 to 600 grms. of rongalite. The crystalline system is rhombic-holohehedral, the ratios of the axes being $a : b : c = 0.8421 : 1 : 0.6783$.

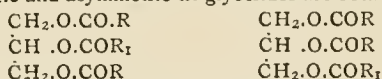
Influence of Silver Nitrate upon the Solubility of Silver Nitrite.—Alex. Naumann and Adolf Röcker.—The authors find that the influence of silver nitrate upon the solubility of the nitrite is not that deduced from van't Hoff's equation expressing the influence of similar ions upon solubility. Even taking into account the incomplete dissociation of the silver nitrate added, a considerable discrepancy still exists. It might be supposed that the formation of double salts is responsible for this discrepancy, but it is highly improbable that such formation would occur to exactly the same extent in all the cases investigated which do not follow the equation, and, moreover, when the process of crystallisation of the mixtures of silver nitrite and nitrate is observed under the microscope, no third salt can be detected. Thus, although the theory of electrolytic dissociation furnishes on the whole a satisfactory explanation of the processes observed, the actual relations found experimentally exhibit discrepancies which have not yet been explained.

Action of Glacial Acetic-hydriodic Acid on Quinones.—K. Lagodzinski.—The author finds that if anthraquinone is suspended in glacial acetic acid, the mixture heated to boiling, and hydriodic acid of specific gravity 1.70 added, the light yellow suspension becomes dark brown, and the anthraquinone goes into solution. On cooling, brown glittering needles separate out. The author has examined several derivatives of anthraquinone, such as alizarin, quinizarin, &c., to see if they also give this reaction, and has found that all these substances, which are difficultly soluble in acetic acid alone, on addition of hydriodic acid, readily give dark brown solutions. Phenanthraquinone and benzil both react similarly with glacial acetic acid and hydriodic acid. The compounds formed have apparently a complicated structure, and in some cases it may be proved that the hydriodic acid takes part in the reaction.

Action of Diazo Compounds upon Primary Aliphatic Amines.—Otto Dimroth.—When diazo compounds react with amines, first of all one molecule of diazonium salt reacts with one molecule of aliphatic amine and triazenes are formed, which are characterised by yielding nitrogen with acids in the cold. The tendency to unite with two molecules of diazo compound is far more strongly developed in the case of the aliphatic amines than with the aromatic bases, and even if the amine is used in considerable excess a large amount of bis-diazo-amine compound is formed. But under suitable experimental conditions, viz., if the triazene is at once removed from the solution, it is possible to check the reaction so that only mono-diazo-amino compound is formed.

Halogen Compounds of Palladium.—A. Gutbier and A. Krell.—In the course of experiments aiming at the determination of the atomic weight of palladium, the authors have prepared some new double salts of palladious chloride and bromide, and have also for the first time obtained derivatives of palladic bromide. They find that ammonium palladious chloride possesses the formula $(\text{NH}_4)_2\text{PdCl}_6$, and thus does not contain a molecule of water of crystallisation; they have obtained the chloropalladates of cæsium and rubidium in the crystalline form, and have converted them into the corresponding derivatives of palladic chloride by treatment of their aqueous solution with chlorine gas. Several double salts of palladious bromide are obtained by the cautious evaporation of mixed solutions of palladious bromide with other bromides, and by the action of bromine vapour upon their aqueous solution the corresponding derivatives of palladic bromide are obtained. Neither palladic bromide nor chloride can be obtained in the pure state. The general formula of the double bromides is Me_2PdBr_6 . They are stable in air, difficultly soluble in cold water, and are decomposed by hot water, bromine being liberated. Concentrated ammonia reduces them to the corresponding bromopalladate, which dissolves in excess of ammonia, and can be converted into palladosamine bromide. All these compounds when cautiously heated in a current of hydrogen give up the whole of their halogen, forming halogen acid.

Synthesis of Fats.—Ad. Grün.—The author has found that it is often best to prepare the glycerides of higher fatty acids by allowing the solution of the fatty acid in concentrated sulphuric acid to act upon the sulphuric acid ester of the glycerin or upon the chlorhydrine. The esterification of glycerin by sulphuric acid (even when great excess of acid is used) ceases with the formation of glycerin disulphuric acid, $\text{C}_3\text{H}_5(\text{OH})(\text{OSO}_3\text{H})_2$, and when organic acids act upon this compound diglycerides are formed, containing two acyl groups. The reaction proceeds very rapidly at a relatively low temperature, and the yield is good, but cannot be made to exceed 70–80 per cent of the theoretical, the action being reversible. No mono- or tri-glycerides appear to be formed, nor were any by-products obtained. Apparently only the two primary hydroxyl groups of the glycerin are esterified, while in α -chlorhydrine the primary and secondary groups are equally easily acted upon, yielding both $\alpha\alpha$ - and $\alpha\beta$ -diglycerides. If the hydroxyl or chlorine is replaced by a fatty acid residue, which differs from the acyl already contained in the molecule, structuro-isomeric pairs of symmetric and asymmetric tri-glycerides are obtained:—



In the author's opinion it must be possible to split up the latter tri-glyceride into optically active components.

MISCELLANEOUS.

The Iron and Steel Institute.—(President: R. A. HADFIELD.—The following is a revised list of the Papers that have been offered for reading at the Sheffield Meeting, September 26–29, 1905:—

- "On the Wear of Steel Rails on Bridges." By Thomas Andrews, F.R.S. (Wortley).
- "On the Metallurgical Department of Sheffield University." By Prof. J. O. Arnold (Sheffield).
- "On the Thermal Transformation of Carbon Steels." By Prof. J. O. Arnold and A. McWilliam (Sheffield).
- "On the Nature of Troostite." By Dr. Carl Benedicks (Upsala).
- "On the Transformations of Nickel Steels." By L. Dumas (Paris).
- "On Steel for Motor-car Construction, and on Vanadium Steels." By L. Guillet (Paris).

- "On the Occurrence of Copper, Cobalt, and Nickel in American Pig Irons." By Prof. E. D. Campbell (Ann Arbor, Michigan).
- "On the Presence of Greenish-coloured Markings in the Fractured Surface of Test Pieces." By Captain H. G. Howorth, R.A. (Sheffield).
- "On Over-heated Steel." By Arthur W. Richards (Grange-town) and J. E. Stead, F.R.S. (Member of Council).
- "On Segregation in Steel Ingots." By B. Talbot (Middlesbrough).
- "On a Manipulator for Steel Bars." By Douglas Upton (Jarrow).
- "On the Influence of Carbon on Nickel and Iron." By George B. Waterhouse (New York).

Members who intend to take part in the discussion will, on notifying such intention to the Secretary, have copies of the papers forwarded to them a week in advance, as far as that may be possible. The Housing Committee of the Sheffield Reception Committee are making arrangements for those members who have stated, on their reply forms, their intention of being present. In view, however, of the unprecedentedly large number of members and ladies who have intimated their intention of attending the meeting, difficulty has been experienced in providing accommodation; and it has, with regret, been found impossible to avoid limiting to some extent the number of ladies. Members are therefore informed that invitations cannot be extended to more than one lady accompanying each member. Full particulars of the meeting may be obtained of Mr. BENNETT H. BROUGH, Secretary, 28, Victoria Street, London, S.W.

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THE CHEMICAL NEWS.

VOL. XCII., No. 2389.

ON THE INFLUENCE OF COLLISIONS AND OF THE MOTION OF MOLECULES IN THE LINE OF SIGHT, UPON THE CONSTITUTION OF A SPECTRUM LINE.*

By Lord RAYLEIGH, O.M., F.R.S.

APART from the above and other causes of disturbance, a line in the spectrum of a radiating gas would be infinitely narrow. A good many years ago (*Phil. Mag.*, 1889, vol. xxvii., p. 298; *Scientific Papers*, vol. iii., p. 258), in connection with some estimates by Ebert, I investigated the widening of a line in consequence of the motion of molecules in the line of sight, taking as a basis Maxwell's well-known law respecting the distribution of velocities among colliding molecules, and I calculated the number of interference-bands to be expected, upon a certain supposition as to the degree of contrast between dark and bright parts necessary for visibility. In this investigation no regard was paid to the collisions; the vibrations issuing from each molecule being supposed to be maintained with complete regularity for an indefinite time.

Although little is known with certainty respecting the genesis of radiation, it has long been thought that collisions act as another source of disturbance. The vibrations of a molecule are supposed to remain undisturbed while a free path is described, but to be liable to sudden and arbitrary alteration of phase and amplitude when another molecule is encountered. A limitation in the number of vibrations executed with regularity necessarily implies a certain indeterminateness in the frequency, that is a dilatation of the spectrum line. In its nature this effect is independent of the Doppler effect—for example, it will be diminished relatively to the latter if the molecules are smaller; but the problem naturally arises of calculating the conjoint action of both causes upon the constitution of a spectrum line. This is the question considered by Mr. C. Godfrey in an interesting paper ("On the Application of Fourier's Double Integrals to Optical Problems," *Phil. Trans.*, A, 1899, vol. cxcv., p. 329), upon which it is the principal object of the present note to comment. The formulæ at which he arrives are somewhat complicated, and they are discussed only in the case in which the density of the gas is reduced without limit. According to my view this should cause the influence of the collisions to disappear, so that the results should coincide with those already referred to where the collisions were disregarded from the outset. Nevertheless, the results of the two calculations differ by 10 per cent, that of Mr. Godfrey giving a narrower spectrum line than the other.

The difference of 10 per cent is not of much importance in itself, but a discrepancy of this kind involves a subject in a cloud of doubt, which it is desirable, if possible, to dissipate. Mr. Godfrey himself characterises the discrepancy as paradoxical, and advances some considerations towards the elucidation of it. I have a strong feeling, which I think I expressed at the time, that the 10 per cent correction is inadmissible, and that there should be no ambiguity or discontinuity in passing to the limit of free paths infinitely long. In connection with some other work I have recently resumed the consideration of the question, and I am disposed to think that Mr. Godfrey's calculation involves an error respecting the way in which the various free paths are averaged.

The first question is as to the character of the spectrum line corresponding to a regular vibration which extends over a finite interval of time. As the energy lying between

the limits u and $u + du$ of frequency (or rather inverse wave-length), Mr. Godfrey finds from Fourier's theorem—

$$\frac{\sin^2 \pi r n}{n^2} dn \dots \dots \dots (1),$$

r denoting the finite length of the train of waves, and n being measured from that value which would be dominant if r were infinitely long. For the total energy of all wave-lengths we have—

$$\int_{-\infty}^{+\infty} \frac{\sin^2 \pi r n}{n^2} dn = \pi^2 r \dots \dots \dots (2).$$

That the total energy should be proportional to r is what we would expect. The maximum coefficient in (1) occurs, of course, when $n = 0$, and is proportional to r^2 ; once proportional to r on account of the greater total energy as given in (2), and again on account of the greater condensation of the spectrum as r increases. Expression (1) may be taken to represent the spectrum of the radiation from a single molecule which describes in a given direction and with a given velocity a free path proportional to r . If there be N independent molecules answering to this description, N may be introduced as a factor into (1). From this expression Mr. Godfrey proceeds to investigate the spectrum corresponding to the aggregate radiation of the gas, integrating first for the different lengths (r) of parallel free paths described with constant velocity, and afterwards for the various component velocities across and in the line of sight, the latter giving rise to the Doppler effect. It is with the first of these integrations that I am more particularly concerned.

In order to effect it, we need to know the probabilities of the various length of free path described with given velocity. "Now, Tait has shown that, of all atoms moving with velocity v , a fraction $e^{-f\rho}$ penetrates unchecked to distance ρ where f is [a function of v and of the permanent data of the gas]". From this we see that, of molecules moving with velocity v , a fraction $f e^{-f\rho} d\rho$ have free paths between ρ and $\rho + d\rho$. Now, such a molecule will emit an undisturbed train of waves of length between r and $r + dr$, where $r = \rho V/v$, and V is the velocity of light. Hence, of all molecules moving with velocity v , a fraction $(f v/V) e^{-v f r/V}$ will give free paths between r and $r + dr$. Returning to the expression (1) for the energy of a single train of length r , we see that with the aggregates of molecules now under consideration (definite thwart and line-of-sight velocities) we have for u a proportion of energy—

$$\frac{f v}{n^2 V} \int_0^\infty e^{-v f r/V} \sin^2 u \pi r \cdot dr,$$

or, on effecting the integration,—

$$\frac{2\pi^2}{4\pi^2 u^2 + v^2 f^2/V^2} \dots \dots \dots (3).*$$

The next steps are integrations over the various velocities, but it is not necessary to follow them here in detail, inasmuch as the objection which I have to take arises already. It appears to me that what we are concerned with is not the momentary distribution of free paths among the molecules which are describing them, but rather the statistics of the various free paths (described with velocity v) which occur in a relatively long time. During this time various free paths occur with frequencies dependent on the lengths. Fix the attention on two of these, one long and one short. They present themselves in certain relative numbers, or say in a certain proportion, and it is with this proportion that we have to do. The other procedure takes, as it were, an instantaneous view of the system, and, surveying the molecules, inquires what proportion of them are pursuing free paths of the two lengths under contemplation. It is not difficult to recognise that this is a different question. Of the paths which are described in a given period of time, an instantaneous survey is more likely to hit upon a long

* Mr. Godfrey's expression (iii.) differs somewhat from (3). A $4\pi^2$ appears to have been temporarily dropped, but this is not material for my present purpose.

* A Paper communicated to the Royal Society.

one than upon a short one. Thus Mr. Godfrey's integration favours unduly the long paths.

The above consideration indicates that we ought to divide by v previously to integration, that is, evaluate—

$$\frac{fv}{n^2V} \int_0^\infty r^{-1} e^{-vr/V} \sin^2 n\pi r \cdot dr \quad (4).$$

If we write—

$$\int_0^\infty r^{-1} e^{-cr} \sin^2 ar \, dr = y,$$

we find—

$$\frac{dy}{da} = \frac{2a}{4a^2 + c^2},$$

and—

$$y = \frac{1}{4} \log \frac{4a^2 + c^2}{c^2}.$$

Hence—

$$(4) = \frac{fv}{4n^2V} \log \left\{ 1 + \frac{4n^2\pi^2V^2}{v^2f^2} \right\} \quad (5),$$

in place of (3).

It must be remarked, however, that an over-valuation of long paths relatively to shorter ones which all correspond to the same velocity, would not of itself explain the 10 per cent discrepancy; for, when the gas is infinitely rare, all the paths must be considered to be infinitely long, and then the proportion of relatively longer and shorter paths becomes a matter of indifference. In fact (3) should give the correct result in the limit ($f=0$), even though it be of erroneous form as respects n , provided a suitable function of f and v be introduced as a factor. If we integrate (3) as it stands with respect to n between the limits $-\infty$ and $+\infty$, we obtain—

$$\frac{2\pi^2V}{vf} \quad (6).$$

But this should certainly be independent of f . I think that if we introduce the factor vf into (3), Mr. Godfrey's analysis would then lead to the same result as is obtained by neglecting the influence of collisions *ab initio*.

It may be convenient to recite the constitution and visibility of a spectrum line according to the simple theory, where the Doppler effect is alone regarded. If ξ be the velocity of a molecule in the line of sight, the number of molecules whose velocities in this direction lie between ξ and $\xi+d\xi$ is, by Maxwell's theory,—

$$e^{-h\xi^2/d\xi} \quad (7).$$

According to Doppler's principle the reciprocal wave-length of the light received from these molecules is changed from Λ^{-1} , corresponding to $\xi=0$, to $\Lambda^{-1}(1+\xi/V)$, V being the velocity of light. If x denotes the variation of reciprocal wave-length, $x=\Lambda^{-1}\xi/V$, and the distribution of light in the dilated spectrum line may be taken to be—

$$e^{-hV^2\Lambda^2x^2/dx} \quad (8).$$

When this light forms interference-bands with relative retardation D , the "visibility" according to Michelson's reckoning is expressed by—

$$\int_{-\infty}^{+\infty} e^{-hV^2\Lambda^2x^2} \cos(2\pi Dx) \, dx \div \int_{-\infty}^{+\infty} e^{-hV^2\Lambda^2x^2} \, dx;$$

that is,—

$$e^{-\frac{\pi^2 D^2}{hV^2\Lambda^2}} \quad (9).$$

If v be the velocity of mean square, on which the pressure of the gas depends,—

$$v^2 = \frac{3}{2h} \quad (10).$$

In terms of v the exponent in (8) is—

$$-\frac{3V^2\Lambda^2x^2}{2v^2} \quad (11),$$

and that in (9) is—

$$-\frac{2\pi^2v^2D^2}{3V^2\Lambda^2} \quad (12).$$

ESTIMATION OF OIL IN WATER FROM CONDENSING ENGINES.

By J. McFARLANE and J. MEARS.

If the oil exceeds 0.4 grain per gallon, use 1 litre for the determination; if below 0.4 grain per gallon, use 2 litres.

Add to 2 litres of the water contained in a 2½-litre flask 5 c.c. of the "ferric chloride" solution and heat up nearly to boiling; then add ammonia in excess, to precipitate the iron (which precipitate contains all the oil), and boil for two minutes.

Allow to stand a few minutes and filter through a 15 c.m. filter-paper which has been previously extracted with ether, washing the precipitate on to the paper with hot water, and washing three or four times with hot water. Then dry the filter and precipitate in the water oven at 100° C. and, when dry, extract with ether in the Soxhlet in the usual way, evaporate the ether extract, and weigh the remaining oil.

Ferric Chloride Solution.—Ten grms. of iron dissolved in 200 c.c. of hydrochloric acid, oxidised with HNO_3 , and made up to 1 litre.

NOTES ON THE ANALYSIS OF DOLOMITE.

By NICHOLAS KNIGHT.

It is well known to analysts that, other things being equal, the simpler and more direct the methods of analysis the better. There is not only a saving of time, but the possibility of loss by the complexity of the processes is diminished. This applies to the trained and experienced chemist, and with especial force to the amateur who is beginning his course in quantitative analysis. The chemical work of the ordinary college student is of necessity so interrupted by his other studies that the direct and simple methods are of peculiar interest and value to him.

In connection with this subject, attention is called to the analysis of dolomite as outlined in the excellent work on Quantitative Analysis by Clowes and Coleman. The writer values the work very highly, and takes pleasure in acknowledging his indebtedness to it in his teaching. We have found that some of the steps directed to be taken in the analysis of this rock can just as well be omitted. The object of this paper is to show that such is the case.

The rock that was studied abounds in Eastern Iowa and in many other parts of the United States. It belongs to the Niagara period, and it is nearly a pure dolomite. It is used extensively as a building stone and in the manufacture of quicklime.

1. *The Insoluble Residue, mainly or wholly Silica, in the Specimens examined.*—According to Clowes and Coleman, after dissolving 1½ grms. of the substance in dilute hydrochloric acid, a little strong nitric acid is added, and the whole is evaporated to dryness on the water-bath in a porcelain evaporating dish. The dish is then heated for an hour in the air-bath to 150° "to convert the silica into the anhydrous insoluble condition." The dish is then allowed to cool, and its contents are heated with a small quantity of strong hydrochloric acid, which dissolves everything except silica and clay. This is filtered and determined.

2. *Another Method for the Insoluble Residue.*—A gm. of the fine powder was weighed into a small beaker, and a little dilute hydrochloric acid was added. The contents of the beaker were gently heated to the boiling-point; the insoluble residue was filtered off, and its weight determined. The following results were obtained:—

Method 1.	Method 2.
0.94 per cent	0.938 per cent
0.87 "	0.87 "
0.89 "	0.88 "

In cases of this kind Method 2 is much shorter, and gives practically the same results as the other. It is therefore to be preferred.

3. *To Determine the Iron and Alumina, Fe₂O₃ and Al₂O₃.*—(A). About 2 grms. ammonium chloride and a little fuming nitric acid are added to the filtrate from the insoluble residue. This is heated to boiling, and the iron and aluminium hydroxides are precipitated with a small excess of ammonium hydrate. The precipitate is quickly filtered off by the use of a pump well washed in hot water, dried, and its weight determined.

(B). According to Clowes and Coleman it is necessary to re-dissolve the well washed precipitate of iron and aluminium hydroxides with hydrochloric acid and precipitate again with ammonia. This double precipitation is necessary, they say, in order to separate completely the small amount of calcium which is precipitated with the iron and aluminium hydroxides. It is not stated why the calcium is precipitated, but all or nearly all ammonia contains more or less ammonium carbonate. This would precipitate the calcium. Yet, while the solution to which the ammonia is added remains acid, ammonium chloride would result from the carbonate, and no calcium could be precipitated. Moreover, the iron present in the solution serves as an indicator by its change of colour, so that no more than a drop or two of ammonia in excess is necessary to be added. The small amount of calcium carbonate that this excess would precipitate, insoluble as it is, is doubtless removed by washing the precipitate sufficiently with hot water. At any rate, the experiment was made a number of times of dissolving the precipitate of iron and aluminium hydroxides with hydrochloric acid and re-precipitating with ammonia. No trace of calcium nor magnesium could be found in the filtrates.

The results obtained by Methods A and B were as follows:—

Al₂O₃ and Fe₂O₃ (per cent).

A.	B.
0.59	0.54
0.55	0.51
0.51	0.48

The calcium was determined by heating the filtrate from the iron and aluminium hydroxides to boiling, and precipitating with the smallest possible excess of ammonium oxalate. Enough of the reagent must be added to insure complete precipitation. This precipitates a small amount of magnesium with the calcium. It is therefore necessary to dissolve the precipitate in warm dilute hydrochloric acid and re-precipitate the calcium with ammonia. This leaves the magnesium in solution.

The two filtrates containing magnesium are united and concentrated to a volume of about 200 c.c. on the water-bath. No difficulty was then experienced in precipitating the magnesium with disodium phosphate and ammonia.

The complete analysis of the specimen resulted as follows:—

	Per cent.
Insoluble residue, mainly SiO ₂	0.87
Fe ₂ O ₃ and Al ₂ O ₃	0.48
CaCO ₃	53.10
MgCO ₃	45.55
	100.00

The carbon dioxide was determined by the Bunsen method.

Clowes and Coleman would precipitate the calcium with a considerable excess of ammonium oxalate, and then evaporate the filtrate from the calcium to dryness, heating further to remove the ammonium salts. "This removal of ammonium salts is necessary, since they prevent the complete precipitation of magnesium." This has not been our experience. A grm. of the original powder will give as accurate results as a grm. and a-half. Some of the precipitates are so large as to be unwieldy with the larger amount of substance.

A second specimen of the dolomite slightly different in composition from the preceding was also studied. The insoluble residue, which was mostly silica, was determined as follows:—

	Method 1.	Method 2.
SiO ₂ (per cent)	0.81	0.95
	—	0.88

The Iron and Aluminium Oxides.

	Method A.	Method B.
Fe ₂ O ₃ and Al ₂ O ₃ (per cent)	2.28	2.43
	—	2.36
	—	2.28
	—	2.26

On dissolving the iron and alumina with hydrochloric acid, and re-precipitating with ammonia, no trace of calcium or magnesium could be found in the filtrate.

The analysis of a similar specimen resulted as follows:—

	Per cent.
CaCO ₃	53.87
MgCO ₃	49.59
Fe ₂ O ₃ and Al ₂ O ₃	2.43
SiO ₂	0.95
	99.84

The author acknowledges his indebtedness to Frances Benson and H. O. Cheney for carrying on the experiments described in this paper.

Cornell College, August 8, 1905.

THE DETERMINATION OF
 THE WAVE-LENGTHS IN THE SPECTRUM OF
 GIESEL'S EMANUM.

By J. HARTMANN.

In my earlier communication on the spectrum of emanium light I expressed the hope that, with a more powerful spectrograph, I should be able to determine more accurately the position of the exceedingly faint lines in the yellow and green parts of the spectrum (*Physikal. Zeit.*, 1904, v., 570). I have now concluded this research, using Giesel's preparation, which has preserved its luminosity unimpaired, and will now describe the result of my measurements.

The spectrograph, S, used for the experiments was most kindly placed at my disposal by Prof. v. Drygalski from the stock of the German South Pole Expedition, for which I had prepared the apparatus. The spectrograph, constructed according to Prof. Scheiner's directions, contains a flint-glass prism of 60° and, as objectives of collimator and camera, two Zeiss's planars of 30 m.m. aperture and 110 m.m. focal length. It thus probably reaches the extreme limit as regards the strength of the light, and is well suited for taking faint spectra; the linear extension of the spectra is indeed so small that, especially in the less refrangible parts of the spectrum, the wave-lengths can be measured only to 1 A.U., which, however, is quite accurate enough in the investigation of such faint spectra. As the apparatus, on account of the quantities of glass in its objectives, absorbs the short wave-lengths strongly, in the investigation of the ultra-violet part of the spectrum I used a very powerful quartz spectrograph, which has recently been described in the *Zeitschrift für Instrumentenkunde* (1905, xxv., 161). The experiments performed with this apparatus are marked Q.

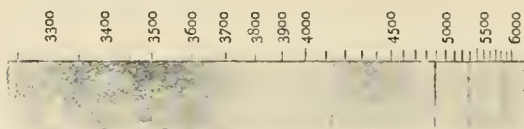
The wave-lengths refer to the measurement of the following six plates:—

Plate S 23	135 hours illumination.
" S 24	191 " "
" S 25	170 " "
" Q 100	36 " "
" Q 101	24 " "
" Q 102	48 " "

λ.	F.	Description.
3250		Commencement of a continuous band.
3560		Maximum intensity of the band.
3810		End of the band.
4070		Commencement of a feebler continuous band.
4340		Maximum of the band.
4720		End of the band.
4137	+3 A.U.	Very faint, fine line.
4743	4	Very faint, fine line.
4885.4	0.1	Principal line; breadth from about 4879—4894.
5287	10	Fainter, very broad line; specially indistinct towards the red, from about 5245—5320. It is probably a double line, the stronger component of which lies at 5272 and the fainter at 5306.
5704	10	Exceedingly faint line, the existence of which is not quite certain.
5838	10	Broad, indistinct line, somewhat fainter than 5287; breadth from 5800 to 5900.

The wave-length previously given by me for the principal line, 4885.4, was completely confirmed by the new measurements, but, on the other hand, the wave-length of the last line, which was previously measured only very roughly, was considerably altered. Moreover, the new experiments have proved with additional certainty the existence of the two lines 4137 and 4743, while the existence of the line 5704, only shown on one plate, still remains uncertain. Under F is given in the table the probable error in the wave lengths.

The accompanying figure shows the whole image of the spectrum (negative).



As regards the interpretation of this spectrum, this could be sought in two directions, according to my opinion which I have already expressed. Firstly, we might assume that a gas mechanically retained by the substance was excited to luminescence by the radiation of the emanation, just as Sir William and Lady Huggins found the band spectrum of nitrogen in the light of radium preparations (*Proc. Roy. Soc.*, 1903, lxxii., 196 and 409). My repetitions of the Huggins' researches have, however, hitherto only given a negative result, for with two different radium preparations, both in air and in hydrogen, I only obtained a continuous spectrum and no trace of a gas spectrum.

Secondly, we might assume that traces of a rare earth held in solid solution in the substance were brought to fluorescence by the radiation. This last supposition has now actually been confirmed by Giesel (*Berichte*, 1905, xxxviii., 775), who has succeeded in producing a fluorescence spectrum, very similar to the spectrum of emanium, by dissolving small quantities of didymium in lanthanum chloride, which also forms the greater part of his emanium preparation.

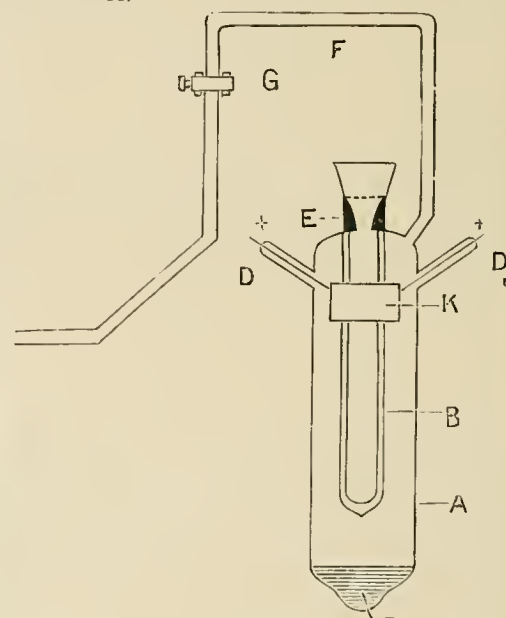
Whether the emanium spectrum is perfectly identical with the didymium spectrum can only be determined by a more accurate measurement of the latter, which presents no difficulty of any kind taking into account the considerably greater strength of light which this possesses on excitation with cathode rays. To render this comparison with the didymium spectrum possible, I considered it desirable to perform the most accurate practicable examination of the emanium spectrum, as it had lost the special physical interest to which the above-mentioned interpreta-

tion of it as a gas spectrum pointed. Nevertheless, it remains a noteworthy phenomenon that a solid body, luminous at a low temperature without external addition of energy, should possess a spectrum which shows, not only fairly sharp lines, but also an intensity maximum situated in the ultra-violet. — *Physikalische Zeitschrift*, vi., No. 13, 401.

A MERCURY ARC LAMP WITH QUARTZ VESSEL SUITABLE FOR CHEMICAL PURPOSES.

By FRANZ FISCHER.

THE mercury arc lamp here briefly described is such as I used for my experiments on the effect of ultra-violet light upon glass (*Berichte*, 1905, xxxviii., 946; and *Physikal. Zeit.*, 1905, vi., 216), and also in my research on the formation of ozone by ultra-violet light (*Berichte*, 1905, xxxviii., 2633).



The figure shows the form of this lamp. It consists of an outer glass vessel A, and an inner double-walled vessel B, which is made of quartz, and is exhausted. The quartz cylinder is fixed into the glass vessel by means of sealing wax. Platinum wires are fused in at D and D₁, and from them is suspended the anode K, an iron ring surrounding the quartz cylinder. F represents the connection with the air-pump, and G is a cock with an oblique bore.

At the bottom of the lamp the mercury for the cathode is placed. The lamp is fixed by means of a rubber ring into the neck of an inverted glass flask. Beneath the rubber ring is a tin-foil ring with copper-wire wound round it to enable the lamp to be lighted by means of an inductor. The lower end of the lamp is immersed in a bowl of mercury. Water circulates through the glass flask to cool it.

The aim of the cooling is to lower the temperature in the interior of the lamp, and thus to obtain a lower density of the mercury vapour, which is favourable to the formation of ultra-violet light. The lamp burns with a bluish violet light.

The anode is connected with the positive pole, and the mercury cathode or bowl with the negative. Moreover, the negative pole of the secondary coil of an inductor is

connected with the mercury and the positive pole is connected with the tin-foil ring. As soon as the inductor is set going the direct current passes through the lamp. The strength of the current usually amounts to 5 amperes, and the potential of the lamp to roughly 20 volts.

Although the quartz vessel is double-walled, and the space between the walls is most carefully exhausted, the inner wall always becomes hot rapidly in consequence of the radiation of heat. To obviate this, a specially constructed glass condenser was inserted into the quartz vessel.—Abridged from *Berichte*, 1905, xxxviii., 2630.

SO-CALLED SOLID SOLUTIONS OF INDIFFERENT GASES IN URANIUM OXIDES.

By CARL FRIEDHEIM.

THE important question as to how helium is retained in the uranium minerals has called forth an interesting paper by V. Kohlschütter and K. Vogdt (*Berichte*, 1905, xxxviii., 1419), in which it is shown that it is possible to prepare an artificial uranium compound which, in the opinion of the authors, may be regarded as an "exact model" of the natural compounds containing helium.

This article induced the author to perform the following experiments, and in order to understand them the gist of article must be given here.

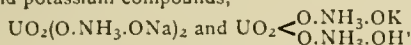
K. A. Kofmann (*Zeit. Anorg. Chem.*, 1897, xv., 75) has prepared a hydroxylamine-ammonia compound of uranic acid, $\text{UO}_4(\text{NH}_4\text{O})_2 + 2\text{NH}_3$, which, when treated with water, gives up ammonia, and yields the substance $\text{UO}_4(\text{NH}_4\text{O})_2 + \text{H}_2\text{O}$, which may be obtained directly from a uranyl salt and excess of aqueous hydroxylamine.

Together with Kohlschütter it was then found (*Zeit. Anorg. Chem.*, 1898, xvi., 463) that the substance possesses an acid character, i.e., the hydroxyl hydrogen of the hydroxylamine residue can be replaced either entirely or partly by ammonium, potassium, or sodium.

Hence the first substance is to be regarded as—



They also succeeded in preparing the neutral sodium and the acid potassium compounds,—



and the correctness of their opinion regarding the nature of the pure hydroxylamine compound was thus supported.*

This canary-yellow coloured compound suffers a change at a high temperature (cf. *Ann. d. Chem.*, 1899, cccvii., 321, et seq.; also *Berichte*, 1905, xxxviii., 1420—1426). If it is strongly heated in a test-tube, it spirts, forming black uranium dioxide, ammonia, and water; *in vacuo* considerable heat is developed, and ammonia and nitrous oxide are formed.

But if it is slowly brought to a temperature of 125° , ammonia and water may be shown to be generated, and after heating for two days a fairly constant decrease of weight takes place, amounting on an average to 17.9 per cent, and a dark yellow to blackish brown mass remains behind, which, when heated in a test-tube, no longer pulverises but gives uranium dioxide, large quantities of ammonia, and water.

The product obtained by heating contains on an average 76 per cent of uranium and 4.95 per cent of nitrogen, besides lower oxide of nitrogen (1 mol. UO_2 to 6—8 mols. UO_3), and, when boiled with caustic soda, gives varying quantities of ammonia (maximum, 1.8 per cent), which are regarded as accidental and negligible.

In dilute acids the preparation dissolves instantly, giving rise to an energetic evolution of nitrogen and nitrous

oxide, the volumes of which are approximately in the proportion of 1 to 2, while the original yellow hydroxylamine compound does not behave similarly.

These facts are explained as follows:—On heating the hydroxylamine uranate to 125° , a slow intramolecular transposition of the hydroxylamine occurs, ammonia and water being formed; these two latter escape; moreover, nitrogen and nitrous oxide are also formed, which remain "practically quantitatively" dissolved in "homogeneous mixture" in the uranic acid, which acts only as an "accelerator" of the reaction.

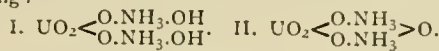
The two gases and the acid "molecularly penetrate" one another, and are examples of "solid solutions of nitrogen and nitrous oxide" in uranic acid; these must decompose with escape of the gases when the solvent is removed, i.e., when the addition of acid converts it into uranyl salt.

Hence the analogy with the behaviour of uraninite and cleveite towards acids, and the authors apparently regard any other explanation of the process occurring on heating the original material and on the decomposition by acids of the product obtained by heating as impossible.

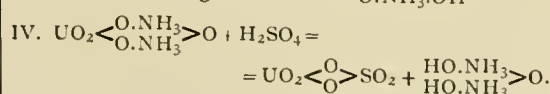
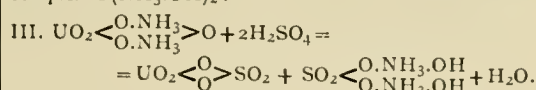
They see also in the product obtained by heating the hydroxylamine uranate a model for the minerals containing helium, although it gives up the "dissolved" gas completely and at a far lower temperature than these on the addition of acids.

It will now be shown that it is possible to explain the process in question in a far simpler manner.

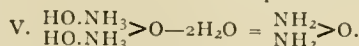
Since, as Hofmann and Kohlschütter (*loc. cit.*) have themselves shown, hydroxylamine uranate (I.) possesses the character of an acid (we may call it hydroxylamine uranic acid), it may by cautious heating be converted into the anhydride (II.), which, mixed with uranic acid,* is present in the dark yellow to blackish brown coloured product of heating:—



This on treatment with acids may not again add on the elements of water† (according to III.), and pass into a mixture of uranyl salt and hydroxylamine salt,‡ but may decompose according to Equation IV. into the first, and a complex $\text{O}(\text{NH}_3.\text{OH})_2$:—



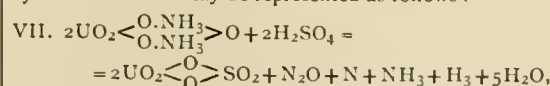
The latter is unstable; first water splits off.



This is the unknown anhydride of hydroxylamine, which is also unstable, and at once decomposes into nitrogen, nitrous oxide, ammonia, hydrogen, and water.



Thus the whole decomposition process of substance II. by means of acids may be represented as follows:—



in which naturally the ammonia cannot escape as such, but remains in solution as primary ammonium sulphate.

* Similar substances are derived from many other acids. Cf. the next reference.

† If we assume that 3 mols. of I. give 1 mol. of II. and 2 mols. H_2UO_4 , the loss of weight must amount to 17.25 per cent, while Kohlschütter and Vogdt find an average of 17.90 per cent. Yet according to the experimental conditions less H_2UO_4 may be present than the amount indicated by the amount of U and N.

‡ Similar cases are known; the difficult change of pyrophosphoric acid and pyrophosphates into the ortho-compounds may be recalled.

† Product I. behaves thus.

Evidently, according to this view, just as Kohlschütter and Vogdt showed, nitrous oxide and nitrogen must escape; but hydrogen must be primarily formed, and its presence was expressly denied by both investigators, and, moreover, ammonia must result, which was certainly found by them, but was regarded as "irrelevant" (see above).

But it may easily be shown that these discrepancies are only apparent, and that Kohlschütter and Vogdt's own researches strikingly confirm the explanation given here.

1. They obtained from their preparation (see above) a maximum of 1.8 per cent ammonia, corresponding to 1.5 per cent nitrogen, and a total of 4.95 per cent N. But for the critical examination of the decomposition process this is not an "irrelevant" amount, but one of considerable importance, which indeed constitutes 0.36 of the total nitrogen, while according to Equation VII. only 0.25 of the total nitrogen appears as ammonia (1 atom from 4 atoms N). Thus the above formula is more than confirmed by this discovery.

2. This excess of ammonia is even an argument in favour of the theory propounded, as evidently one part of the hydrogen first formed combines with the nascent nitrogen to form ammonia.

3. Since it was further expressly stated by Kohlschütter and Vogdt that some uranium trioxide is reduced in the process of solution, the reducing action of the nascent hydrogen evidently manifests itself in this way also, and thus the absence of hydrogen in the gaseous mixture can be explained quite easily.

4. According to the statements of the authors the volumes of the nitrogen and nitrous oxide evolved are approximately in the proportion of 1 to 2. This is also required according to Equation VII.

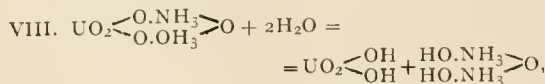
5. As was also stated (*loc. cit.*, p. 1423), hydroxylamine phosphate is decomposed in an exactly similar manner as is here deduced for the uranate, namely (at 130°), into ammonia, nitrous oxide, nitrogen, hydrogen, and a very little oxygen; a further confirmation of the view put forward.

These arguments deduced from Kohlschütter and Vogdt's own results in favour of the theory advanced here may be supplemented by the following:—

1. It was originally the intention of the author to determine whether the product which results on heating hydroxylamine uranate to 125° could be decomposed by water under pressure, so that a larger quantity of the nitrogen present was converted into ammonia. The existence of a solid solution of nitrogen or nitrous oxide in uranic acid would thus be made in the highest degree improbable.

But to my great surprise it was found that the preparation was decomposed by water slowly in the cold, and very quickly at 100°, a fact which has hitherto apparently escaped observation. Gases escape in this case also, but were not further investigated, and ammonia is also formed; when the experiment is suitably arranged this ammonia does not escape, but remains behind as ammonium uranate.

Thus a decomposition process occurs analogous to that shown in IV.



and the uranic acid combines with the ammonia formed according to VI.

This provides an explanation of the otherwise inexplicable fact that on the distillation with caustic soda of the product obtained on heating, which (*cf.* Formula II.) contains no ammonia, the same quantity of nitrogen in the form of ammonia is found as after dissolving it in acids (*cf.* Equations VII. and VIII.), and this behaviour agrees only with the theory here put forward.

(a). 1.8082 grms. of the preparation dried at 120° were heated for several hours with water, with an upright condenser connected with the boiling flask; on account of the

spiriting of the solid residue towards the end, the heating must proceed very cautiously. The crystalline structure is then lost, and the colour becomes more canary-yellow. The exit end of the cooling tube is kept during the whole operation in air-tight connection with a vessel containing 10 c.c. of N/2 H₂SO₄. The contents of this vessel required on titration 50 c.c. N/10 NH₃; thus no trace of ammonia had escaped. The residue in the flask gave on distillation with 33 per cent caustic soda 1.94 per cent NH₃.

(b). 1.7875 grms. of the same preparation were distilled directly with 33 per cent caustic soda. Result, 2 per cent NH₃.

(c). 1.5640 grms. of the same specimen were dissolved in dilute sulphuric acid, and then the distillation with 33 per cent soda was performed. 2.06 per cent NH₃ was found. Both in (b) and (c) 10 c.c. N/2 H₂SO₄ were used, and the ammonia absorbed was determined by titration of the excess of acid with N/10 NH₃.

These results show the correctness of the above statements, and were confirmed when the experiments were repeated. But the results obtained, which always agreed with the same test, as with (a), (b), and (c), varied with different preparations, giving from 1.47 to 1.71 per cent NH₃.

Thus in this case also the amount of ammonia nitrogen varies just as it was proved by Kohlschütter and Vogdt, (*loc. cit.*, p. 1422), and just as, generally speaking, the analytical values* given by them were also found with the author's preparations.

2. The decomposability of the product proved under 1 argues against the assumption of Kohlschütter and Vogdt that a solid solution of nitrogen and nitrous oxide is present in it. For how could the water withdraw the solvent from it? Like sulphuric acid, which dissolves it, *i.e.*, the uranic acid?

The action can be regarded as a chemical action only in the sense of Equation VIII., and as a proof of the existence of the anhydro-compound II.

In conclusion, one more point must be emphasised from the experiments of Kohlschütter and Vogdt. On heating their preparation *in vacuo* they obtain not only the "dissolved" gases nitrogen and nitrous oxide, but also oxygen in quantities, which vary greatly according to the temperature and pressure applied. This behaviour "apparently contradicting," as they say themselves, "the whole assumption of a solution" is most simply explained by the assumption here made that the whole complex, according to the experimental method—on heating rapidly with acids or under lower pressure—can split up in different ways.

We know that the decomposition of the mother-substance, hydroxylamine, may vary essentially, according to the conditions of the experiment, which, moreover, is easily understood if we bear in mind the simultaneous presence of the group NH₂ on the one hand, and also of the group NOH.

The interesting article of Kohlschütter and Vogdt suggests many experiments; it would be very interesting, for instance, to investigate the behaviour of the anhydro-compound when warm towards hydrogen, sulphuretted hydrogen, and towards reduction agents, working in the dry way, on fusing. But I have expressly refrained from this because I wish to avoid any encroachment upon the authors' field of research.

I only wish to show that structural-chemical considerations, which are in complete agreement with our ideas on valency and with other views, can explain the question at least as satisfactorily as the theory—supported by experimental results—of the "existence of a solid solution of nitrous oxide and nitrogen in uranic acid," and of the "existence of a model corresponding to the minerals containing helium," which is said to result on heating hydroxylamine uranate to 126°.

* The gas analysis experiments were not repeated for the reason given at the end.

I owe hearty thanks to cand. phil. Paul Schulz for his valuable help in preparing specimens and performing analyses.—*Berichte*, 1905, xxxviii., 2352.

A RAPID VOLUMETRIC METHOD FOR THE DETERMINATION OF PHOSPHORIC ACID.*

By W. B. HIRT and F. W. STEEL.

RECOGNISING the necessity for a rapid, and at the same time accurate, method for the determination of phosphoric acid in fertilisers and similar phosphatic materials, particularly in connection with the manufacture of chemical manures, we have lately devoted some considerable time to an examination of various volumetric processes.

The original Pemberton method and its modifications were tried, but discarded in favour of the method described below.

The method described by Dr. Littmann, (*CHEMICAL NEWS*, vol. lxxx., p. 178, or *Chemiker Zeitung*, vol. xx., No. 68), we find, with some alterations, to be one which fulfils the desired conditions, viz., rapid, accurate, easy, and not involving the use of expensive reagents.

The presence of more than very small amounts of bases precipitable by sodium hydrate is detrimental; such precipitates are not always completely dissolved by the sodium citrate, and consequently they obscure the end-points in the titrations.

Practically the only interfering base met with in manures is calcium, and it is most conveniently removed as sulphate; other reagents, such as oxalic acid and ammonium oxalate, were tried for the removal of calcium, but the results proved unsatisfactory. Varying intensity in the light affects the appearance at the end-points of the titrations; strong direct light should be avoided, a moderate steady illumination ensuring regular results.

Organic matter must not be present in sufficient amount to impart a yellow colour to the solution to be titrated. It is best removed by direct ignition; its removal by such means as ignition with magnesium or potassium nitrates is undesirable, as impurities, which may exert a baneful influence upon the work, are thus introduced. Ignition with ammonium nitrate has a tendency to result in mechanical loss. A fact which appears to be common to all volumetric methods for determination of phosphoric acid also obtains in this method, viz., that when comparatively large amounts of phosphoric acid are present in the solution, the results of analysis show greater divergence from those obtained by the gravimetric method than when small amounts of phosphoric acid are present.

Therefore we recommend that when the phosphoric acid in any material exceeds 20 per cent, the weight of the substance used for the determination should be 0.125 gm., while when it is under 20 per cent, 0.25 gm. should be used.

In the former case the c.c.'s. of special soda solution (*vide infra*) required for neutralisation must of course be multiplied by 2 to get the percentage.

The following special reagents are required in addition to the ordinary ones mentioned in the description of the process.

1. Sodium hydrate (approximately normal solution).
2. Sodium hydrate, special. Made by diluting 35.22 c.c. of strictly normal sodium hydrate solution to 1000 c.c. with water. When 0.25 gm. of material is used each c.c. of this solution represents 1 per cent phosphoric anhydride, P_2O_5 .
3. Sulphuric acid solution, corresponding exactly with the special soda solution.
4. Sodium citrate solution 25 per cent (*vide infra*).

5. Acid mixture (A), composed of:—Sulphuric acid conc., 250 c.c.; nitric acid conc., 150 c.c.; and water 100 c.c.

6. Acid mixture (B), composed of:—Sulphuric acid conc., 60 c.c.; nitric acid conc., 100 c.c.; and water 140 c.c.

All reagents must be free from carbonic anhydride, CO_2 .

The sodium citrate solution is prepared as follows:—110 grms. sodium hydrate sticks are placed in a beaker of about 1500 c.c. capacity; 192 grms. of pure crystallised citric acid, $C_6H_5O_7 \cdot H_2O$, are next added, then about 300 c.c. water. A very violent reaction takes place, in consequence of which the temperature rises to 103° C. when the solution boils, so expelling any carbon dioxide which may be present. Now dilute the solutions slightly and boil for a few minutes to ensure complete expulsion of carbon dioxide.

As the amount of sodium hydrate used is insufficient to neutralise all the citric acid, the solution will now be acid. The beaker is covered and allowed to stand until quite cold, about 2 c.c. phenolphthalein solution added, then with constant stirring, sufficient of a solution of sodium hydrate, free from carbonic anhydride, to produce a faint pink colour; make up to 1032 c.c. (sp. gr. = 1.151) with water, and store in a well stoppered bottle. The addition of about 1 c.c. of ethyl ether to this solution assists in its preservation. The solution is neutralised when required as follows:—The amount likely to be used during the day's work (say 200 to 300 c.c.) is drawn off (filtering through cotton-wool if necessary). 10 c.c. of this is diluted to about 40 c.c. (if the original solution is alkaline, the pink colour of the phenolphthalein appears at once on dilution through ionisation taking place), 0.25 c.c. phenolphthalein added, then standard (N 10) acid or alkali till neutral; from this titration the amount of acid or alkali required for the remainder of the 200 or 300 c.c. of the solution is calculated and added thereto, another 10 c.c. then drawn off and checked for neutrality.

In the above titration vigorous shaking of the flask is necessary.

The acid mixtures are so proportioned that the minimum excess of free acid is left after solution of the phosphate, anything more than a slight excess being very undesirable.

The Working Process.

1. *Phosphoric Anhydride Soluble in Water*.—2 grms. are washed on a filter with water (200 c.c.) in the usual manner. In order to prevent precipitation of calcium phosphate in the solution, about 1 c.c. of sulphuric acid (10 per cent) is added when about 50 c.c. of washings have collected. Any slight precipitate of calcium sulphate may be neglected. Titrate 25 c.c. (= 0.25 gm.) directly, according to directions for total phosphoric acid.

So far as our present experience goes, the amount of soluble organic matter present has been too small to effect this determination in any way.

2. *Phosphoric Anhydride Insoluble in Water and Ammonium Citrate*.—The residue obtained after extraction with water and then ammonium citrate (neutral sp. gr. 1.09) is ignited to a white ash, treated with 5 c.c. of acid B, heated until fumes of sulphuric acid are given off, made up to 100 c.c. with water, and 25 c.c. (= 0.5 gm.) titrated as in (3). Burette reading is divided by 2 to give percentage of phosphoric anhydride.

3. *Total Phosphoric Anhydride*.—2 grms. weighed out. In the absence of organic matter, treat with 5 c.c. acid A at once. Where organic matter is present the 2 grms. of substance are placed in a porcelain dish and heated in the muffle for a few minutes, so that organic matter is carbonised; it is not necessary to incinerate completely, free carbon not being objectionable.

Now transfer the ignited substance to a small beaker, add 5 c.c. acid A, cover the beaker and heat for a few minutes on the sand-bath, remove cover of beaker and continue heating until white fumes of sulphuric acid are

* From the *Proceedings of the Society of Chemical Industry of Victoria*, March–April, 1905.

copiously evolved; cool, dilute with water, again cool and wash into a 200 c.c. gauged flask, using about 150 c.c. water; add from 30 to 40 c.c. absolute alcohol (to throw down as much calcium sulphate as possible), then add water to 200 c.c. mark, mix well, and either allow to clarify by subsidence or filter through a dry filter. Titrate 25 c.c. (= 0.25 gm.), *vide infra*. Methylated spirits purified by distillation from sodium hydrate may be used instead of absolute alcohol. After considerable practice the use of alcohol may be omitted, but better results will be got by its use.

The Titration.—This operation requires special care and should be carried out in strict accordance with the following directions.

To the solution obtained as above, add 3 drops methyl orange solution (an excess of methyl orange must be avoided, as it tends to interfere with the end-point in the second titration). Add approximately normal soda solution till nearly neutral (it may be necessary to add 1 or 2 drops more methyl orange), finish off with N/10 soda. Should the end-point be overshoot, titrate back with N/10 sulphuric acid. Now add 10 c.c. sodium citrate solution, and 0.25 c.c. phenolphthalein solution, and titrate with the special soda solution until the usual pink tint appears. The burette reading gives the percentage of phosphoric anhydride directly. N/10 soda may be used in place of the special solution; this is not recommended, however, as there is a very much greater risk of error, the special soda being much more dilute. If N/10 soda be used the factor for 0.25 gm. of substance is 2.84, giving percentage of phosphoric anhydride, P_2O_5 . The factor for 1 gm. is 0.71.

A few results comparing the above method with the gravimetric are appended:—

	Percentages of phosphoric anhydride.	
	Volumetric.	Gravimetric.
1. Superphosphate (non-nitrogenous)	23.61	23.59
2. Superphosphate (nitrogenous)	21.65	21.53
3. Bone-dust and superphosphate (mixed)	23.20	23.31
4. Bone-dust	22.12	22.51
5. Bone-meal	25.84	25.92
6. Rock guano	38.81	38.83

Nos. 1 to 5 inclusive. Gravimetric method employed was precipitation as ammonium magnesium phosphate in presence of ammonium citrate.

No 6. Gravimetric method employed was American official molybdate method.

While experiments on the molybdate volumetric methods were in progress, we tried a variety of filters, endeavouring to find one which would enable the yellow precipitate to be conveniently dealt with. The one which we found most satisfactory consists of a layer of pulped filter-paper. It was our intention to deal more fully with this matter of filtration, but in a recent number of the *Journal of the American Chemical Society* (vol. xxvii., p. 287, March, 1905), Shimer describes his work along the same line, simultaneously arriving at the same conclusion as we have, so that we need only refer those interested to the above paper. Shimer finds that the filter constructed according to his directions may be used for a great variety of precipitates. One difference between Shimer's filter and that used by us, is that for some precipitates we find it convenient to use an ordinary funnel into which a perforated disc of aluminium about 15 m.m. diameter, and having a piece of wire of the same metal attached as a handle, is fitted; the felt of paper is laid on about 2 m.m. thick by suction. The precipitate and paper pulp can be very easily washed into the titration flask, by raising the disc slightly by means of the wire handle and directing upon it a jet of water from a wash-bottle.

We desire to express our thanks to Mr. J. Cuming, jun.,

for permitting the publication of the results of our investigations.

Chemical Laboratory, Cuming, Smith, & Co. Pty., Ltd.,
Yarraville, Melbourne, Australia.

Note added July 4, 1905.—Further experiments, with a view to the simplification of the process, are in progress. The following additional comparative figures, between this method and the U.S.A. Official Gravimetric method, show the accuracy obtainable:—

	Percentages total P_2O_5 .	
	A.O.A.C. molybdate.	Volumetric.
Non-nitrogenous superphosphate	20.26	20.16
Non-nitrogenous superphosphate	20.59	20.73
Nitrogenous superphosphate	23.13	23.08
Bone-dust	21.62	21.58

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY OF NEW SOUTH WALES.

General Monthly Meeting, June 7th, 1905.

H. A. LENEHAN, F.R.A.S., President, in the Chair.

THE following report was presented by Prof. LIVERSIDGE at the Annual General Meeting, May 3rd, 1905:—

International Catalogue of Scientific Literature.

In 1903, I was appointed by the Council of this Society, acting as the Regional Bureau for New South Wales, to represent this State at the Council Meetings held in London in May last. I duly attended the meetings, and now have the honour to make the following report:—The Royal Society of London commenced the work by compiling Catalogues of Scientific Papers (printed between 1800 and 1883) in twelve large quarto volumes, the first volume of which was issued in 1867. In it the titles are arranged solely under the authors' names. A catalogue of the papers published since, *i.e.*, between 1884 and 1900, is now in hand, and a subject index is also nearly completed.

The possibility of preparing a complete catalogue of current scientific literature was considered by the Royal Society in 1893, but as it was apparent that the work was beyond the resources of the Royal Society, or indeed of any single body, the Society sought the opinion of representative foreign bodies and individuals, and the replies being favourable, steps were taken to summon an International Conference. This conference, at which I was present as a Delegate, took place in London on July 14th to 17th, 1896, and was attended by delegates appointed by the Governments of Canada, Cape Colony, Denmark, France, Greece, Hungary, India, Italy, Japan, Mexico, Natal, the Netherlands, New South Wales, New Zealand, Norway, Queensland, Sweden, Switzerland, the United Kingdom, and the United States. It was then unanimously resolved to compile and publish a complete catalogue of current scientific literature, arranged both according to subject matter and authors' names. The Royal Society was requested to appoint a committee to further consider the system of classification to be adopted and other matters, and it was decided to establish a Central Bureau in London.

At the second International Conference held in London on October 11th to 13th, 1898, several questions were settled, and a provisional International Committee appointed which afterwards met in London on August 1st to 5th, 1899, when the work was still further expedited and the Royal Society requested to organise the Central Bureau, and make all necessary arrangements so that the preparation of the catalogue might be commenced in 1901.

A third International Conference was held in London on June 12th and 13th, 1900, at which all financial and other difficulties were removed by the Royal Society agreeing to act as publishers and to advance the funds necessary to start the enterprise. The supreme control over the catalogue is now vested in an International Convention which is to meet in London in 1905, in 1910, and every tenth year afterwards, to re-consider, and if necessary to revise, the regulations for carrying out the work of the catalogue. In the interval between two successive meetings of the Convention the administration of the catalogue is carried out by the International Council, the members of which are appointed by the Regional Bureaus.

The total expenditure from July 1st, 1900, to February 20th, 1904, has been £10,153, and the total amount received from subscribing bodies was £6755; eventually the publication will pay its way, but it may be some time before the debt to the Royal Society will be extinguished. The financial support given by the different countries is shown in the following list. New Zealand has now become a contracting body:—Austria, £165; Canada, £119; Cape Colony, £109; Denmark, £102; Egypt, £17; Finland, £45; France, £754; Germany, £901; Greece, £34; Holland, £133; Hungary, £68; India and Ceylon, £471; Italy, £459; Japan, £255; Mexico, £85; New South Wales, £34; New Zealand, £17; Norway, £85; Nova Scotia, £17; Orange River Colony, £17; Poland, £17; Portugal, £17; Queensland, £34; Russia, £512; South Australia, £34; Sweden, £85; Switzerland, £119; United Kingdom, £765; United States, £1251; Victoria, £17; Western Australia, £17. Total £6755.

It has been suggested that special efforts should be made by the Regional Bureaus to bring the catalogue under the notice of scientific workers, and to secure an increase in the number of subscribers. The whole of the first and second issues of the International Catalogue of Scientific Literature have been published with the exception of the volumes on botany and zoology; the third annual issue is in preparation, and several of them are already in the press. The number of entries in the author-catalogue of the first annual issue was 43,447, and the total number of entries in that issue was 149,768. The numbers of books and papers indexed in the volumes of the second annual issue are as follows:—(A) Mathematics, 1843; (B) Mechanics, 841; (C) Physics, 2433; (D) Chemistry, 5632; (E) Astronomy, 1223; (F) Meteorology, 1988; (G) Mineralogy, 1307; (H) Geology, 1702; (J) Geography, 2022; (K) Palæontology, 638; (L) General Biology, 689; (M) Botany, 6339; (N) Zoology, 7131; (O) Anatomy, 1424; (P) Anthropology, 1861; (Q) Physiology, 9671; (R) Bacteriology, 3132. The total number of entries in the author-catalogue of the second annual issue is therefore 49,876, an increase of 6429, or about 15 per cent more than the number in the first annual issue. The total number of pages in the first annual issue is 8387.

The accompanying table shows the number of slips received and the instalments in which they were supplied to the Central Bureau.

It was originally intended that the catalogue should not only contain the titles of papers, but that their subject-matter should be fully indexed also; financial considerations have, however, led to the number of subject-entries being at present limited in number. The title slips received at the Central Bureau very often showed that the papers were insufficiently indexed, especially in the lists of new species in botany, zoology, and chemistry; in many cases the Central Bureau has made good these deficiencies. The Executive Committee urge that efforts should be made in all countries to supply fuller information as to the contents of papers; if this were done the catalogue would be much more complete and the cost would be much decreased, and all Journals are urged to index each paper and attach the registration numbers at the time of publication.

At the meeting of the International Council held at the Royal Society's House, London, May 23rd and 24th, 1904, it was resolved, in consequence of the success achieved by

Germany	146,552	slips in	59 instalments
France	46,792	"	38 "
United Kingdom . .	43,484	"	166 "
United States . . .	37,688	"	68 "
Russia	21,071	"	5 "
Italy	13,473	"	25 "
Holland	6,657	"	17 "
Austria	6,379	"	2 "
Poland	3,492	"	8 "
India and Ceylon . .	2,231	"	39 "
Japan	2,208	"	10 "
Switzerland	1,932	"	7 "
Hungary	1,745	"	4 "
Denmark	1,722	"	17 "
Sweden	1,457	"	4 "
Victoria	1,445	"	3 "
Norway	1,303	"	12 "
New South Wales . .	1,016	"	5 "
Finland	707	"	8 "
South Africa	645	"	4 "
Belgium	584	"	2 "
Canada	537	"	11 "
New Zealand	327	"	3 "
South Australia . . .	130	"	4 "
Western Australia . .	16	"	1 instalment
	343,503		522 instalments

the International Catalogue of Scientific Literature, and of its great importance to scientific workers, to recommend that its publication be continued. The agreement with the contracting countries was made in the first instance for five years only, in case the publication of the catalogue should fail financially, or in other ways. It was also decided to spend £100 in making the catalogue known, and to take steps to invite the co-operation of other countries not yet represented on the Council, e.g., Spain, the Balkan States, South American Republics, &c.

The proposal to publish additional volumes upon—(a) Medicine and Surgery; (b) Agriculture, Horticulture, and Forestry; (c) Technology (various branches) was discussed, and it was decided that the Executive Committee should take the suggestion into fuller consideration, and bring it under the notice of the International Convention in July, 1905. It was also resolved that all alterations in the schedules should be collected and edited by the Central Bureau prior to submission to the Regional Bureaus for their opinions, and that the schemes should be edited by a special committee before being submitted to the International Convention.

(Signed) A. LIVERSIDGE.

The following paper was read:—

"On the so-called Gold-coated Teeth in Sheep." By A. LIVERSIDGE, LL.D., F.R.S., Professor of Chemistry, University of Sydney.

Paragraphs have appeared recently in some of the London and Sydney newspapers, stating that gold-coated teeth have been found in Australian sheep. I have recently received the lower half of a sheep's jaw-bone from Dubbo, the teeth of which are more or less completely incrustated with a yellow metallic substance, but more like iron pyrites (marcasite) or brass than gold. The deposit is about $\frac{1}{2}$ of an inch, or less than 1 m.m. in thickness. Under a half inch objective it is seen to be made up of thin translucent layers, but there is no recognisable organic structure. The metallic lustre is due to the way in which the light is reflected from the surface of the superimposed films. The scale partly dissolves in dilute acids. The residue consists of filmy organic matter, still possessing a metallic sheen although white in colour instead of yellow. The chemical examination shows that the incrustation on the teeth is merely a tartar-like deposit made up principally of calcium phosphate and organic matter.

Note.—Prof. Liversidge also showed a calculus of a similar metallic-looking character from a sheep's stomach,

deposited in distinct layers round a piece of twig, but of rather a darker bronze tint than the substance on the teeth. This specimen belongs to the Sydney Technological Museum, and was kindly lent for exhibition by the Curator, Mr. R. T. Baker.

NOTICES OF BOOKS

Atlas of Emission Spectra of most of the Elements. By AUGUST HAGENBACH, Ph.D., and HEINRICH KONEN, Ph.D. Authorised English Edition by ARTHUR S. KING, Ph.D. Jena: Gustav Fischer. London: William Wesley and Son. 1905.

This atlas contains heliographic reproductions of photographs of the spectra of all the elements with a very few exceptions, taken by the authors with a small Rowland grating. Twenty-eight charts are given, showing all lines separated which have an interval of $0.8 \text{ A.U.} = 0.08 \mu\mu$, and though naturally the charts cannot reproduce the full detail of the actual photographs, the technical difficulties occurring in their preparation have been most successfully surmounted, and the work will be found of great value in the laboratory. Only the strongest lines outside the sensitive region are given, owing to the impossibility of obtaining both the actinic part and the limiting region on the same plate. The charts are accompanied by descriptive notes pointing out the material used, and the impurities present, and emphasising those features which are actually to be seen in the charts, either with the naked eye or with a lens; a chapter of useful spectrographic notes is also added. The translation has been made from the proof-sheets of the German edition, and every effort has been made to ensure the accuracy of the wave-lengths, which have been checked as far as possible by the original tables.

Analyse Chimique Minérale. Choix de Méthodes. ("Inorganic Analysis. Selected Methods"). By EUG. PROST. Paris and Liège: Ch. Béranger. 1905.

THE aim of this book is to collect all that is indispensable for the analytical chemist, to enable him to cope with the analysis of samples of the most common substances met with in practice. Under the headings of the individual metals and acid radicals, the characteristic reactions, methods of qualitatively demonstrating the presence, and a selection of methods of determination and separation of the ions are given. The introduction contains a short description of elementary processes and operations, which seems to suggest that the author had in view the needs of beginners, for whose use, however, we should not recommend the book. No attempt is made to provide a course of graduated difficulty, and in many cases the directions are not sufficiently explicit for students. Moreover, in a book for beginners, hints are required to show how time may be economised to the utmost, and also special pitfalls and sources of error should be pointed out. For the benefit of the analyst some elementary matter might have been replaced by a greater choice of methods; for instance, in a case of such importance as the separation of chlorides, bromides, and iodides it would have been better to give a description of additional processes.

CHEMICAL NOTICES FROM FOREIGN SOURCES

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 6, August 7, 1905.

Calcium Chloroborates.—L. Ouvrard.—The natural mineral boracite can be artificially manufactured. Analogous compounds can also be formed in which the magnesium is replaced by iron, zinc, cadmium, &c., and the chlorine by bromine or iodine. The author describes in this paper the products which he prepares by the substitu-

tion of calcium for the magnesium, and of which the preparation presents a certain interest. He separates the chloroborate, $5\text{B}_2\text{O}_3 \cdot 3\text{CaO} \cdot \text{CaCl}_2$, in the form of prismatic crystals, which are insoluble in water and dilute acetic acid, but easily decomposed by the stronger acids, even when very dilute. He also prepares the compound $3\text{B}_2\text{O}_3 \cdot 3\text{CaO} \cdot \text{CaCl}_2$, which presents a totally different appearance.

Constitution of Disymmetric Diparaditolylethane, Dihydride of 2.7.9.10-Tetramethylantracene, and 2.7-Dimethylantracene.—James Lavanx.—The author establishes the fact that, if he uses the same constants as those used by Anschütz in his experiments (*Liebigs Annalen*, ccxxxv., p. 313) on tetramethyl anthracene hydride containing the groups CH_3 in 2.7.9.10, his own carbide B, which is prepared by removing the methyls 9 and 10, is the 2.7-dimethylantracene.

Absorption Spectrum of Manganese Salts.—P. Lambert.—To determine the absorption spectrum of any substance, it has to be purified as far as possible from foreign bodies. To this end, the author purified a solution of manganese dioxide in nitric acid by a large number of precipitations, according to Beilstein's method. The pure dioxide thus prepared is dissolved in hydrochloric acid free from iron. This chloride gives a very characteristic absorption spectrum, consisting of bands between the following wave-lengths:—

I.	Between λ 557.50	and λ 513.00
II.	" 442.50	" 420.00
	a. " 412.25	" 410.25
	b. " 408.00	" 405.25
III.	c. " 403.25	" 402.06
	d. " 401.00	" 400.00
	e. " 397.75	" 396.25
	f. " 395.75	" 394.50

The author does not believe that manganese alone presents this spectrum, but he intends to further investigate the matter.

QUEEN'S COLLEGE, GALWAY.

THE MATRICULATION EXAMINATION OF SESSION 1905-1906 commences on OCTOBER 19th. Matriculation Certificates of any University within the United Kingdom are accepted.

All Lectures, Scholarships, Exhibitions, and Prizes, are Open to Students of either sex.

The Scholarship Examinations in Arts, Medicine, and Engineering commence on OCTOBER 19th.

DEPARTMENTS OF SCIENCE, MEDICINE, & ENGINEERING.

Mathematics	Prof. THOMAS JOHN IANSON BROMWICH, M.A., late Fellow of St. John's College Cambridge; Examiner, R.U.I.
Physics	Prof. A. ANDERSON, M.A. (Camb.), Hon. LL.D. (Glasgow), late Fellow of Sidney Sussex Col- lege, Cambridge; Member of the Senate of the Royal Uni- versity of Ireland.
Chemistry	Prof. ALFRED SENIER, Ph.D., Berlin.
Natural History, Mineralogy, and Geology	Prof. RICHARD J. ANDERSON, M.A., M.D., M.R.C.S. Eng.
Engineering	Prof. EDWARD TOWNSEND, M.A., D.Sc.
Electrical Engineering	Mr. CHARLES C. PLUMBE, B.Sc. (London Faculty of Engineering).
Anatomy and Physiology	Prof. JOSEPH P. PYE, M.D., M.Ch., D.Sc., F.R.U.I.
Practice of Medicine	Prof. JOHN ISAAC LYNNHAM, M.D., M.Ch., M.A.O., F.R.U.I.
Surgery	Prof. W. W. BRERETON, L.R.C.S.I., M.R.C.P.I.
Materia Medica	Prof. NICHOLAS W. COLOHAN, M.D., M.Ch.
Gynaecology	Prof. RICHARD J. KINREAO, B.A., M.D., L.R.C.S.I.

Prospectus of the Courses and Regulations for Scholarships, &c., can be had on application to the—

REGISTRAR,
Queen's College, Galway.

THE CHEMICAL NEWS.

VOL. XCII., No. 2390.

(STUDENTS' NUMBER).

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree in this University must either have passed the Matriculation Examination in this University, or be admitted under the Statute which provides that the Senate may admit graduates of or persons who have passed the examinations required for a degree in other Universities approved by it. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, &c., are open to Women upon exactly the same conditions as to Men.

There are three Examinations for Matriculation in each year; commencing on the second Monday in September, January, and June (or July, as may hereafter be determined).

Every candidate entering for the Matriculation Examination must pay a Fee of £2. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following five subjects:—(1) English; one paper of three hours. (2) Elementary Mathematics; two papers of three hours each. (3) Latin or Elementary Mechanics, or Elementary Physics—Heat, Light, and Sound, or Elementary Chemistry, or Elementary Botany; one paper of three hours in each subject. (4) and (5) Two of the following subjects, neither of which has already been taken under Section (3); one paper of three hours in each subject; if Latin be not taken, one of the other subjects selected must be another Language from the List, either ancient or modern:—Latin, Greek, French, German, Arabic, Sanskrit, Spanish, Portuguese, Italian, Hebrew, Ancient History, Modern History, Logic, Physical and General Geography, Geometrical and Mechanical Drawing, Mathematics (more advanced), Elementary Mechanics, Elementary Chemistry, Elementary Physics—Heat, Light, and Sound, Elementary Physics—Electricity and Magnetism, Elementary Biology—Botany, Elementary Biology—Zoology. Candidates in subjects marked with asterisk must give at least two months' notice before the commencement of the Examination.

A Pass Certificate, signed by the Principal, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

Several valuable Scholarships and Exhibitions are available to students.

INTERMEDIATE EXAMINATION IN SCIENCE.

The Intermediate Examination in Science will commence on the second Monday in July.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. This Examination will consist of two printed papers and a practical examination.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. EXAMINATION.

The B.Sc. Examination will be held on the fourth Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously, and to have passed the Matriculation Examination at least three years previously. In the years 1905 and 1906 only, candidates will be enabled to pass this Examination without the prescribed knowledge of French and German.

The Fee for this Examination is £5.

Examination for Honours.

For the examination for Honours in Chemistry candidates are required to show a general acquaintance with General Theoretical Chemistry, Chemistry of Carbon Compounds, Physical Chemistry, and History of Chemistry since the time of Boyle.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

DOCTOR OF SCIENCE.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

PRELIMINARY SCIENTIFIC (M.B.) EXAMINATION.

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the second Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

The Fee for this examination is Five Pounds.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. Odling, F.R.S.
Lee's Reader in Chemistry—G. Brereton Baker, M.A.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, W. W. Fisher, M.A., J. Watts, M.A., and J. E. Marsh, M.A.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—G. D. Liveing, M.A., F.R.S.
Jacksonian Professor of Natural and Experimental Philosophy—Sir J. M. Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in any term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

A graduate of another University may be admitted as an 'advanced' student, and obtain a degree after two years' residence in the University.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science in King's, Trinity, St. John's, St. Peter's, Clare, Trinity Hall, Queen's, Jesus, Christ's, Emmanuel Sidney, Pembroke, Caius, and Downing Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar*.

UNIVERSITY OF DUBLIN. TRINITY COLLEGE.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.
Professor of Applied Chemistry—Emil A. Werner, F.C.S., F.I.C.

Demonstrator—W. C. Ramsden, F.C.S.

The general Quantitative and Research Laboratories include working accommodation for about 130 Students. The Laboratories will open on the 2nd of October. Lectures will commence about November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The Lectures delivered are:—

1. *Inorganic Chemistry and Chemical Philosophy*.—Elementary, first year; Advanced Inorganic Chemistry, second year; Physical Chemistry, third year.
2. *Organic Chemistry*.—General, second year; advanced, third year.
3. *Metallurgy*.—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of *Practical Chemistry for Medical Students* begins during the first week in April and terminates about the end of June.

A special course for Dental Students will be given.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

By recent decrees, Prizes in Chemistry and Physics will be given in future at the October (Arts) Entrance Examination, and also at the Terminal Examinations of the Junior and Senior Freshmen Years.

Similarly, two Science Scholarships will be obtainable by Undergraduates, and tenable for five years. These Foundation Scholars receive £20 per annum, have free commons, their chambers for half the charge paid by other students, and their tutorial fees are at one-fourth the usual rates.

KING'S COLLEGE.

(DIVISION OF ENGINEERING AND APPLIED SCIENCE).

Professor of Chemistry—J. M. Thomson, F.R.S., F.C.S.
Assistant Professor—Herbert Jackson, F.C.S.

Lecturer and Demonstrators—P. H. Kirkaldy, F.C.S., D. Northall Laurie, F.C.S., S. W. Collins, and L. Hinkel.

The Academical Year consists of Three terms. The days fixed for the Admission of New Students in the Academical Year 1905-1906 are Oct. 4, Jan. 9, and April 30.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *visu voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Chemical Analysis, both by liquid tests and the blowpipe, analysis of ores, liquids, &c., and Elementary Volumetric Analysis.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry: Winter Session, £5 5s.; Summer Session, £3 3s.; Course, £8 8s. Practical Chemistry: Winter Session, £5 8s.; Summer Session, £4 4s. Experimental and Analytical Chemistry—Five days a week: One month, £4 4s.; Three months, £10 10s.; Six months, £18 18s.; Nine months, £26 5s. Three days a week: One month, £2 12s. 6d.; Three mos., £6 6s.; Six mos., £11 11s.; Nine mos., £15 15s.

METALLURGY.

Professor—A. K. Huntington, A.R.S.M., F.I.C., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

Fee, £3 3s. for the Course.

PHOTOGRAPHY.

Lecturer—Prof. J. M. Thomson, F.R.S., F.C.S.

For particulars apply to Prof. Thomson.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the Winter Session.

UNIVERSITY COLLEGE.

FACULTY OF SCIENCE.

Professors—Sir William Ramsay, K.C.B., LL.D., F.R.S. (Inorganic and Physical Chemistry); J. Norman Collie, Ph.D., F.R.S. (Organic Chemistry).

Assistants—E. C. Baly, F.I.C.; J. K. H. Inglis, B.Sc., M.A.; N. T. M. Wilsmore, M.Sc.; and S. Smiles, D.Sc.

The Session is divided into three Terms, as follows:—First Term, from October 3 to December 20; Second Term, from January 9 to March 30; Third Term, from May 1 to June 16. Class Examinations begin June 18.

Introductory Course of Inorganic Chemistry.

Tuesday and Thursday, at 9. Practical, Friday, 2 to 3.30, or 3.30 to 5. Fee, £10 10s.

This Course treats of the chief physical and chemical characters of the Non-metallic Elements, their preparation and characteristic tests.

Junior Course of Inorganic Chemistry.

First and Second Terms: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

In this Course the physical principles bearing on Chemistry are first discussed, and the Chemistry of the Elements and their compounds is treated in considerable detail, under the headings—Elements; hydrides, halides, oxides, sulphides, &c., borides, carbides and silicides, nitrides, phosphides, &c., and alloys. Special attention is devoted to substances of commercial importance. The concluding Lectures are devoted to Physical Methods and their bearing on Chemical Problems.

Third Term: Lectures will be given on Mondays and Fridays at 9 and on Wednesdays at 11, on the chief types of Carbon Compounds.

Fees:—For the Course, £7 7s.; for the First or Second Terms, £4 4s.

A Practical Class will meet throughout the Session.

Senior Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9, beginning in January.

The Principles of Chemistry will be specially considered, comprising the Atomic Theory, Chemical Classification, the Periodic Law, Thermal Chemistry, Dissociation, the Application of Physical Methods to the Solution of Chemical Problems, and the influence of Mass and Temperature on the progress of Reactions. Special attention is paid to the most recent Chemical Theory researches.

Third Term: Some Lectures will also be given on Saturdays at 9, during the Third Term, on the History of Chemistry.

Fee:—For the Course, £3 3s.; for a Term, £2 2s.

Organic Chemistry.

Mon., Wed., and Fri., at 9, during the session.

This Course is suitable for Students who intend to study Chemistry from a scientific standpoint. No previous knowledge of Organic Chemistry is expected of those attending the Class, which should, however, be taken concurrently with the preceding Course, and with Practical Organic Chemistry in the Laboratory.

Fee:—For the Course, £6 6s.; for a Term, £2 12s. 6d. for a Second Course, £3 3s.

An Advanced Course will be held twice a week throughout the Session for those engaged in prosecuting research in Organic Chemistry. Fee, £5 5s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Analytical and Practical Chemistry.

The Laboratories are open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Courses qualify Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. Several valuable Scholarships are available to students.

ROYAL COLLEGE OF SCIENCE AND
ROYAL SCHOOL OF MINES.

Professor of Chemistry—W. A. Tilden, D.Sc., F.R.S.

Assistant Professor—M. O. Forster, Ph.D., D.Sc.

Demonstrators—H. Chapman Jones; G. T. Morgan, D.Sc., A.R.C.S.; and J. C. Philip, M.A., Ph.D., B.Sc.

Assistants—G. S. Newth and Miss Whiteley, D.Sc., A.R.C.S.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Board of Education. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the Royal School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. Students who are not candidates for the Associateship are permitted to enter as occasional students in one or more special branches of science. The Associateship of the Royal College of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, and Geology, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction lasts for three years, is the same for all the divisions during the first year, after which it is specialised according to the particular division in which the student is working for the Associateship.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first year, and, in the second and third year, those subjects prescribed as necessary for the division in which he seeks to obtain his Associateship. A student who goes through the prescribed course of instruction in any subject except Mining and Metallurgy and passes the necessary examinations receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
Chemistry	£ 3	£ 13
Physics	5	12
Biology with Botany .. .	5	12
Geology with Mineralogy ..	4	8
Mechanics	4	6
Metallurgy	2	13
Mining	4	

The fee for the course of Mine Surveying is £10.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to £40.

The Session is divided into two Terms. The first Term begins about the first week of October, and ends about the middle of February. The second Term begins in the middle of February, and ends about the middle of June.

The hours of study are from 10 a.m. to 1.15, and from

2 to 4 or 5 p.m. every day, except on Wednesday and Saturday, when the College closes at 1 p.m.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 250 teachers are admitted to them, and they receive third class railway fare to and from South Kensington, and a sum not exceeding £3 towards their expenses.

THE SCHOOL OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Sixty-fourth Session will commence on Oct. 2, 1905.

Professors—Chemistry, Arthur W. Crossley, D.Sc., Ph.D., F.I.C. (Dean); Botany, J. Reynolds Green, Sc.D., F.R.S., F.L.S.; Pharmaceutics, Henry G. Greenish, F.I.C., F.L.S.

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also of those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies.

Prospectuses and further information may be obtained from the Dean of the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH. UNIVERSITY OF WALES.

Professor—J. J. Sudborough, D.Sc. (Lond.), Ph.D. (Heidelberg), F.I.C.

Assistant Lecturers and Demonstrators—A. Brooke, Ph.D. (Strass.), and T. C. James, B.A. (Cantab.), B.Sc.

Lecturer in Agricultural Chemistry—J. Alan Murray, B.Sc. (Edin.).

Lecturer on Dyeing—(Vacant).

The College is open to male and female students above the age of sixteen years. The Session commences on Oct. 3rd, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Intermediate Science Course; four lectures weekly throughout the Session. (2 and 3) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, three lectures weekly on General and Physical Chemistry. (Courses A and B will generally be given in alternate Sessions; for 1905-1906, Course A). (4 and 5) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly during the Michaelmas and Lent terms.

Laboratory Courses.—The Laboratories are open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays. Regular Courses of practical work, suitable for the B.Sc. degree of the Universities of London and Wales, or for the Associateship of the Institute of Chemistry, can be followed. Facilities are given for Students wishing to undertake research work. Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 12s. 6d. per term, and for twelve hours, 25s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 15, and exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A CONSTITUENT COLLEGE OF THE UNIVERSITY OF WALES.

Chemistry.—Professor, K. J. P. Orton, M.A., Ph.D., F.I.C. Assistant Lecturer and Demonstrator, Alice E. Smith, B.Sc. Assistant Lecturer in Agricultural Chemistry, Alan Baguley, B.Sc., F.I.C. Junior Demonstrator, Edward Jones, B.Sc.

Physics.—Professor, E. Taylor Jones, D.Sc.

The Session opens October 3rd, 1905. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the Matriculation Examination of the University of Wales. Fee for the Session £3 3s.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £3 13s. 6d.

B.Sc. Course.—Inorganic and Physical Chemistry. Fee for the Session, £3 3s.

Agricultural Chemistry.—Fee, £2 2s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. Students are prepared for the First Examination of the Conjoint Board of the Royal Colleges of Surgeons and Physicians. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor—C. M. Thompson, M.A., D.Sc., F.C.S.

Assistant Professor—E. P. Perman, D.Sc., F.C.S.

Demonstrator—R. D. Abell, D.Sc.

The Session commences October 3rd, and terminates on June 29th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 50 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of about 80 lectures held during the Lent and Summer terms in continuation of the Junior Course; together with laboratory practice it forms the qualifying course for the Intermediate Examination of the University of Wales, and will cover the subjects required for the Intermediate Examination in Science of the University of London. Fee, £4 4s.

The Senior Course consists of about 80 lectures on Organic Chemistry; Fee, £3 3s.

A course of 20 lectures on Qualitative Analysis and a short course on Organic Chemistry will also be given.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held, and practical instruction in Dry Assaying will be given in the Metallurgical Laboratory, which is fitted with the necessary furnaces and apparatus.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £2 2s. per term; twelve hours, £3 3s. per term; eighteen or more hours, £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students wishing to graduate at a Scottish University, or preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry—Morris W. Travers, D.Sc., F.R.S.

Assistant Professor—Francis E. Francis, D.Sc., Ph.D.

Lecturer—Oliver C. M. Davis, B.Sc., A.I.C.

Lecture Assistant—J. H. Sturgess.

The session 1905-1906 will begin on October 3. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical

and electrical laboratories. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the College. Several Scholarships are tenable at the College. Full information may be obtained from the Registrar.

DAY LECTURES.

Inorganic Chemistry.

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Elementary Course.—Three Lectures a week will be given during the Session. Fee, £3 13s. 6d.

Special Course.—A special course of Lectures is also given to Elementary Teachers.

General Course.—Three Lectures a week will be given throughout the Session. Fee, £3 13s. 6d.

Advanced Course.—Two Lectures a week will be given throughout the Session. Fee, £3 13s. 6d.

Organic Chemistry.

General Course.—Three Lectures a week will be given throughout the Session. Fee, £3 13s. 6d. An advanced course of lectures will also be given one day a week during the session. Fee, £2 2s.

Practical Chemistry.—Laboratory Instruction.

The Chemical and Metallurgical Laboratories will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it will be closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, Metallurgy, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. Fees in Guineas—

Days per Week	Five.	Four.	Three.	Two.	One.
Per Session ..	15	12½	10	7½	5
" Two Terms ..	11	9	7½	5½	3½
" One Term ..	7	6	4½	3½	2½

Students may arrange to divide their days of laboratory work into half-days.

Chemical Scholarship.—Among others, a Chemical and a Metallurgical Scholarship each of £25 are offered for competition.

EVENING LECTURES.

A course of Lectures, which is subject to variation to suit the requirements of Students, will be delivered during the First and Second Terms. Fee 7s. 6d.

Pharmaceutics.—During the first and second Terms a course of Lectures will be given one evening a week dealing chiefly with the *Materia Medica*, Pharmacy, and Chemistry of the British Pharmacopœia. Fee, £1 1s.

Practical Chemistry.—Laboratory Instruction.—The Laboratory will be open one evening a week from 6 till 9. Instruction will be given in Qualitative and Quantitative Analysis, and in the Preparation of Chemical Products. Fees:—Two Terms, 21s; One Term, 12s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

The Calendar of the College, price 1s. (post-free, 1s. 4d.), containing detailed information of the various Courses, may be obtained on application to the Registrar.

MERCHANT VENTURERS' TECHNICAL COLLEGE, BRISTOL.

CHEMISTRY AND METALLURGY.

Professor—J. Wertheimer, B.Sc., B.A., F.I.C., F.C.S.

Lecturers—G. P. Darnell Smith, B.Sc., F.I.C., F.C.S.;

H. A. M. Borland, A.R.C.S.; E. E. Elt, B.Sc.

Demonstrators—E. H. T. Parker; P. W. Alloway;

C. D. Fuller.

Assistants in Chemical Laboratory—H. E. Phipps and J. H. Leonard.

The Laboratories of this Department are open during the Term on every week-day as a School of Practical Chemistry, Analysis, and Assaying, to Students of either sex. They include the Junior Laboratory (or forty Students working at one time), Senior Laboratory, Balance Room, Combustion Room, Store Rooms, Metallurgical Laboratory, and Research Laboratory. Each Student works independently, and receives individual instruction and help.

The training in this Department is intended to fit Students to become Professional Chemists, to prepare them for Medical or Pharmaceutical examinations in Chemistry, to instruct them in the branches of Applied Chemistry required in Manufactures and Agriculture, and to train them in practical Metallurgical processes, especially Assaying.

Special facilities will be given to Students wishing to undertake research work approved by the Principal; and the Courses provide completely for the Prel. Sci. Examination (M.B.), and for the Examinations in Chemistry for the B.Sc. and D.Sc. degrees of the University of London.

The three years' course at this College in the subjects of Theoretical and Practical Chemistry, Theoretical and Practical Physics, and Elementary Mathematics, is accepted by the Council of the Institute of Chemistry as satisfactory evidence of the training of candidates for the Associateship of the Institute.

Certificates of Proficiency in Assaying will be given to Students who complete a Course of not less than two years' work in the Metallurgical Department, and pass satisfactorily the College examinations in the Theory and Practice of Assaying.

The Laboratories are open every week-day from 9 till 12 noon, and from 1.30 to 4.30 p.m., except Saturday, when they close at noon.

The Annual Fee of £10 10s. secures (in addition to the use of either or both Laboratories) permission to attend the Lectures in Physics and Mathematics as well as Chemistry, and to use the Physical Laboratory and the Engineering Workshop.

The College Day Classes re-open on Sept. 19, and the Evening Classes commence on Monday, October 2.

Further detailed information may be obtained from the College Calendar, price 6d., or the Prospectus for Day or Evening Classes (free).

UNIVERSITY OF BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., M.Sc., LL.D., F.R.S.

Assistant Lecturers and Demonstrators—Alex. McKenzie, M.A., D.Sc., Ph.D.; Alex. Findlay, M.A., D.Sc., Ph.D.; T. S. Moore, B.A.; C. K. Tinkler, B.Sc.

The Session will be opened on October 2nd, 1905.

Lecture Courses.

First Year.—A. This part of the course is arranged (1) to give a full exposition of the general principles of Chemical Science, (2) for the systematic study of the properties of the more important elements and their compounds, and (3) to indicate the chief applications of Chemistry in the Arts and Manufactures. Four hours weekly during the Winter and Spring terms. Mondays to Thursdays inclusive, at 9.30 to 10.30 a.m. Fee, £5 5s. B. This part of the course includes an introduction to the study of Organic Chemistry, with a description of the properties, relations, and methods of preparation of the more important groups of Carbon Compounds. Three hours weekly during the Summer term. Mondays, Wednesdays, and Fridays, at 9.30 to 10.30 a.m. Fee, £1 11s. 6d.

Second Year.—*Advanced Organic Chemistry.*—This course extends over two years, and is divided into two parts:—(a) Carbon Compounds of the Fatty Series; (b) Aromatic and other Cyclic Compounds. Only one of these parts will be taken in each year. The class meets twice weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. *General and Physical Chemistry.*—This course will deal in outline with the more recent developments of Theoretical Chemistry. The class meets once weekly by arrangement during the three terms. Fee, £1 11s. 6d.

Third Year.—A further Course in Advanced Organic Chemistry will deal with one of the above parts of the Course. The class meets two hours weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. A further Course on General and Physical Chemistry, in which special subjects attracting attention at the time receive treatment. Fee, £1 11s. 6d.

Practical Chemistry.

The instruction in Practical Chemistry extends over three years. The Laboratory will be open daily from 9.30 to 5, except Saturdays, when it closes at 1 p.m. Fees—

	All day.	Three hours per day.	Three hours per day; five days a week.	Three hours per day; three days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term . .	7	4½	4	2½
Two Terms . .	13	8½	7½	5
Three Terms	18	12	11	6½

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Special facilities are given to Advanced Students for the prosecution of original research.

Metallurgy.

There is a separate University department for Metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in June.

Ascough Scholarship.—One Open Scholarship of the value of about £30 is awarded annually in July.

Bowen Scholarship.—One Open Scholarship in Metallurgy, value about £96, is awarded annually in June.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

CITY OF BRADFORD TECHNICAL COLLEGE.

DEPARTMENT OF CHEMISTRY AND DYEING.

Head of Department—Prof. W. M. Gardner.

Lecturers in Chemistry—B. North, A.R.C.Sc. (Lond.)

L. L. Lloyd, Ph.D.; S. F. Stell, F.C.S.

Demonstrators in Chemistry—S. R. Illingworth and N. E. Scale.

Lecturer in Physics—J. A. Tomkins, A.R.C.Sc. (Lond.).

Demonstrator in Physics—E. B. Walker.

Lecturer in Dyeing—A. B. Knaggs, F.C.S.

Demonstrator in Dyeing—L. Minikin.

Lecturer in Gas Manufacture—W. Cranfield.

Lecturer on Botany, Biology, and Pharmacy—W. West, F.L.S., Ex. Pres. Yorkshire Naturalists' Union.

The following courses of instruction are provided:—

I. *General Chemistry Course*, extending over four years, including Lectures in Inorganic, Organic, and Technological Chemistry, Principles of Analysis, Technical Analysis, Physical Chemistry, Crystallography, Fuels, Lighting and Ventilation, Physics, Mathematics, Mechanics, with Laboratory work in Chemistry, Physics, Bacteriology, and Microscopy.

II. *Chemistry and Dyeing*, extending over four years. Includes most of the above subjects, along with Lectures and practical work in Dyeing, Colour matching, &c.

III. *Chemical Engineering*. Three years' course, preparing Students for positions in Chemical Works, Sewage Works, &c.

IV. *Sanitary Science*. One year's Course, recognised by the Sanitary Institute as preparing for their certificate examination. Subjects: Chemistry, Physics, Sanitary Engineering, Sanitary Law, Building Construction, Drawing, Physiology, and Bacteriology.

V. *Dyeing*. Extending over one or two years.

VI. *Textile and Dyeing*. Arranged for those Students who desire to study the two subjects simultaneously.

VII. *First Professional Examination, Conjoint Medical Board* (M.R.C.S., L.R.C.P.), London.—Attendance at the College and College Certificates in Chemistry, Physics, and Biology are recognised by the Conjoint Board for Medical Studies as a qualifying curriculum.

VIII. *General Pharmaceutical Course*. Prepares for the Minor and Major Pharmaceutical Examinations. Each extends over two years on three half-days per week, and includes Chemistry and Physics, Botany, Biology, Materia Medica, Pharmacy, and Dispensing.

IX. Attendance at the College Courses and College Certificates in Chemistry, Physics, Animal Biology, and Botany are recognised by the Conjoint Board for Medical Studies.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

CHEMICAL DEPARTMENT.

Professor—Prof. E. Kinch, F.C.S., F.I.C.

Assistant—W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

THE UNIVERSITY OF LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc., F.R.S.

Professor of Organic Chemistry—Julius B. Cohen, Ph.D., B.Sc.

Lecturer on Physical Chemistry—H. M. Dawson, B.Sc., Ph.D.

Assistant Lecturers and Demonstrators—C. E. Whiteley, M.Sc., and W. Lowson, B.Sc., F.I.C.

Demonstrator—W. H. Perkins, B.Sc.

The Session begins October 4, 1905.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £4 4s.

2. Advanced Inorganic Chemistry.—Metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. Advanced Inorganic Chemistry.—Non-metals. Tuesday, Thursday, and Saturday, at 9.30 a.m. Fee, £3 13s. 6d.

4. Organic Chemistry.—Tuesday, Thursday, and Saturday at 12 noon. Fee £3 13s. 6d.

5. Honours Courses.—(a) Organic Chemistry: Monday, Wednesday, and Friday at 12 noon in the First and Second Terms; fee, £2 12s. 6d. (b) History of Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the First Term; fee, £1 11s. 6d. (c) Physical Chemistry: Tuesday, Thursday, and Saturday at 9.30 a.m. in the Second and Third Terms; fee, £2 12s. 6d. (d) Electro-chemistry: One hour weekly; 31s. 6d.

Laboratory Courses.

The University Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session.—Students working six days per week, £21; five, £18 18s.; four, £16 16s.; three, £13 13s.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 from January to March. Fee, £5 5s.

Elementary Science for Teachers.—Saturdays, 9.30 to 12.30, for half the session. £2 12s. 6d.

Dyeing and Tinctorial Chemistry Department.

Professor—Arthur G. Green, M.Sc., F.I.C.

Lecturer and Research Assistant—A. G. Perkin, F.R.S., F.I.C.

Assistant Lecturer—A. B. Steven, B.Sc.

The Courses extend over periods of three or four years, and are intended for those who wish to obtain a full scientific and practical education in the art of dyeing, &c. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, e.g., the sons of manufacturers, calico printers, managers, master dyers, &c.

Leather Industries Department.

Professor—H. R. Procter, M.Sc., F.I.C.

Assistant Lecturer and Demonstrator—F. Kopecky.

Demonstrator—Harold Brumwell.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—R. S. Seton, B.Sc.

Lecturer in Agricultural Chemistry—C. Crowther, M.A., Ph.D.

The full Course occupies two years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture.

Research Students are admitted to the University Laboratories on reduced terms.

Several valuable Fellowships and Scholarships are at the disposal of the University, viz., the Salt, Akroyd, Brown, Baines, Emsley, Craven, Wheatley, Leeds City Council, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The North, East, and West Ridings County Council's Scholarships are tenable at the University of Leeds.

UNIVERSITY OF LIVERPOOL.

Professor of Chemistry—J. Campbell Brown, D.Sc.

Professor of Physical Chemistry—F. G. Donnan, M.A., Ph.D.

Lecturer on Organic Chemistry—A. W. Titherley, D.Sc., Ph.D.

Demonstrators and Assistant Lecturers—A. T. de Moulpied, M.Sc., Ph.D.; F. J. Brislee, M.Sc.; A. Rule, M.Sc., Ph.D.; and E. Garratt, M.Sc.

Assistant—H. H. Froyssell.

The Session commences October 1st.

Entrance Scholarship Examination takes place early in May each year.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in the University of Liverpool; for Degrees in Medicine of Liverpool; for the Pharmaceutical, Veterinary, Dental, and Public Health Diplomas; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry and other Examination Boards.

Lecture Courses.

A. General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £4.

Pharmacy Courses: Junior, £3; Senior, £3.

Course B.—Metals and Non-metals. Fee, £3.

Course C.—Inorganic Chemistry. Fee, £3.

Course D.—Organic Chemistry. Fee, £3.

Course E.—Special Organic Subjects. Fee, £2.

Course F.—Physical Chemistry. Fee, £2.

Course G.—Advanced Physical Chemistry. Fee, £2.

Course H.—History of Chemistry and Chemical Philosophy. Three Terms. Fee, £2.

Courses I.—Applied Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) General Principles of Metallurgy. (3) Iron, Steel, and Aluminium. (4) Copper, Lead, Silver, and Gold, and other Metals. (5) Distillation of Coal and Tar Industries. (6) Fuel and Gas. (7) Chemistry Applied to Sanitation. (8) Technical Gas Analysis. (9) Applied Electro-chemistry. Three terms. Fee, each course £1 10s.

Practical Classes.

(1) Junior. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances; preparation of Inorganic Compounds. (3) Revision Class. (4) Senior: Practical Organic. (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Sanitary subjects, Examination of Water and Air, &c.

Chemical Laboratory.

The Chemical Laboratories recently enlarged provide accommodation for every kind of chemical and metallurgical work and research. They include thirty rooms devoted to the study of Chemistry and Metallurgy. Separate rooms are provided for Organic Work, Quantitative Analysis, Water Analysis, Gas Analysis, Photometry and Photography, Electro-chemical Work, Metallurgy Laboratories, a Research Laboratory, and a Museum. New stores for students' apparatus and chemicals have also been provided and placed in charge of a skilled dealer.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided.

TABLE OF FEES.

Per Week.	One Term, Three Months.	Three Terms One Session.
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Whole week	10 10s.	21

Pharmaceutical Course (see special syllabus).

D.P.H. Course (see special syllabus).

Course for Dental Degree (see special syllabus).

Technological Curriculum.

Preliminary Year.—Chemistry, the Elementary Course. Practical Classes 1 and 2. Mathematics, or Mechanics, Elementary Engineering, Drawing, and Design (in this or one of the following years). German.

First Year.—Chemistry—Courses B and D; Chemical Laboratory three days per week; Technological Chemistry, Course J. Physics, with laboratory work, one day per week. Mathematics (intermediate). German. Engineering, part of First Year Course. Intermediate B.Sc. Examination may be passed.

Second Year.—Chemistry, Lecture Courses C and F, Technological Chemistry, Course J. Chemical Laboratory, four days per week. Engineering, Mathematics, or Physics (Advanced). The Final Examination for the B.Sc. Degree of the University of Liverpool, or the Inter. Exam. of the Institute of Chemistry, may be taken.

Third Year.—In the third year the student should begin to specialise. The following are possible alternatives:—1. Courses G, H, and J. Any other Courses omitted in a previous year. Laboratory, five days per week. The Degree of B.Sc. in the Honours School of Chemistry may be taken. 2. Metallurgical Classes. Metallurgical Laboratory, two days per week. Chemical Laboratory, Gas Analysis, and Electro-chemistry, two days per week. Physical and Electrotechnical Laboratory, one day per week. 3. Courses F, H, and J. Physics (Senior Course). Chemical Laboratory, four days per week. Physical Laboratory, one day per week. 4. Courses F and I, and a course on Chemistry applied to manufacturing operations. Chemical Laboratory, three or four days per week. Engineering Laboratory and Electrotechnical Laboratory, one day per week.

Students may finally choose a special subject either of research or of applied Chemistry. The Final Examination for the Associateship of the Institute of Chemistry may be taken after 1, 2, or 3. Those who have taken the Ordinary Degree of B.Sc. may pass the M.Sc. Examination in any subsequent year.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1906, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the College Secretary not later than November 15, 1906. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes, including laboratory work, will be held during the winter.

The Prospectus containing particulars may be obtained from the Secretary, University of Liverpool.

ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE.

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S.

Lecturer in Chemistry—F. C. Garrett, M.Sc., F.C.S.

Lecturer in Agricultural Chemistry—S. Hoare Collins, F.I.C., F.C.S.

Assistant Lecturer and Demonstrator—J. A. Smythe, M.Sc., Ph.D.

Demonstrator—A. A. Hall, M.Sc., Ph.D.

First Year Courses.—1. *General Course.*—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on

Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 4th. Fee, £3 10s. for the Session.

11. *Special Course*.—More advanced than the above. Wednesdays and Fridays, 11 to 12. Fee, £3 10s. for Session.

For Diploma in Electrical Engineering.—Tuesday, 12 to 1. A course of Lectures will be given dealing with the Principle of Chemistry, Fuel, the Phenomena of Combustion, and Metals and Alloys employed in Engineering, &c. Fee for the course, £2.

Second Year Courses.—The Lectures for the second year students consist of a course of Lectures on Organic Chemistry, and a course of Lectures on Inorganic Chemistry. The class on Organic Chemistry will meet on Tuesdays and Thursdays at 11 a.m., and will commence on October 3rd. The class for Inorganic Chemistry meets at 11 a.m. on Mondays. Fee for Session, £3 10s.; for Inorganic alone £1 10s.; and for Organic alone £3.

Third Year Courses.—Advanced Classes are held for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s.

A Lecture Course in Analytical Chemistry will be given on Fridays, at 9.15 a.m. Fee for the course, £1.

Metallurgy and Assaying.—Lecturer, Professor Louis, M.A., F.I.C., F.C.S.; Demonstrator, H. Dean, A.R.C.M. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees*.—Student working two days, £3 10s. per term, £9 per session; one day per week, £2 per term, £5 per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the degree of Bachelor in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in the following subjects:—Arithmetic; English Essay; Geometry; the subject-matter of Euclid, Books I., II., III.; Algebra, up to and including Quadratic Equations. Also any two of the following:—English Language; Latin, including Grammar and Easy Sentences; Greek; French; German; Geography. The next examination commences on September 25. Names to be sent in at least ten days before this date. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the three following examinations:—1. The first examination for the Degree of B.Litt. 2. Durham Examination for certificate of proficiency in General Education, held in March and September. 3. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Bachelorship in Science.—Every candidate for the Bachelorship in Science will be required to satisfy the examiners in Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year, and at the end

of the third year in an examination in one chief and two auxiliary subjects. For details of the subjects the College Calendar should be consulted. Candidates may qualify for the degree of B.Sc. by attending special courses in Agriculture, Engineering, and Mining, and passing the several examinations.

Exhibitions.—Two Exhibitions of the value of £20 and £10 respectively will be awarded in September next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Monday, September 25th.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Several valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year, which is open to Bachelors of Science of any British University; the examination for this Scholarship will be held during the week commencing September 25th. Candidates should send in their names to the Secretary on or before September 19th.

THE UNIVERSITY OF MANCHESTER.

Professor and Director of the Chemical Laboratory.—Harold B. Dixon, M.A., M.Sc., F.R.S.

Professor of Organic Chemistry.—W. H. Perkin, Ph.D., F.R.S.

Lecturers and Demonstrators.—G. H. Bailey, D.Sc., Ph.D.; D. L. Chapman, B.A.; Norman Smith, M.Sc. *Assistant Lecturers and Demonstrators*.—D. Trevor Jones, M.Sc.; C. H. Burgess, M.Sc.; E. C. Edgar, B.Sc.; C. Weizmann, Ph.D.

Lecturer in Organic Chemistry.—J. F. Thorpe, Ph.D.

Lecturer in Metallurgy and Fuel.—W. A. Bone, D.Sc., Ph.D., F.R.S.

Lecturer in Electro-Chemistry.—R. S. Hutton, D.Sc.

The Session begins on October 4, 1905.

The Chemical Classes form part of the Courses for Degrees in the University.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during the Lent Term.

These courses are intended for Medical Students and others commencing the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30, during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, and Fridays, at 2, during the two Winter Terms. The Metals.

Third Year Honours Course.—At times to be arranged. Short Courses in Theoretical and Physical Chemistry.

Organic Chemistry (General).—Mondays and Fridays, at 9.30, during the two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Wednesdays, at 9.30, during the two Winter Terms.

History of Chemistry.—Thursdays, at 9.30, during the two Winter Terms.

Metallurgy.—Introductory Course, followed by either—(A) Lead, Copper, Bismuth, Antimony, Zinc, and Tin; or (B) Iron and Steel. Each Course, one Lecture per week during the Session.

Electro-chemistry.—General Theoretical Course: Two hours per week during the Michaelmas Term.

Applied Electro-chemistry: One hour per week during Lent and Easter Terms. A course of six lectures on the Electric Furnace and its Applications will be given on Saturday afternoons during the Michaelmas Term.

Applied Chemistry.—(1) Sulphuric Acid and Alkali Manufactures; General Principles of Chemical Engineering. (2) The Natural and Artificial Colouring Matters and the Principles of Dyeing and Printing. (3) The Chemistry of Fuel; the Manufacture of Illuminating Gas and Gaseous Fuel.

Chemistry Laboratory Courses.

During the first year, the student works in the "Roscoe" or the "Dalton" Laboratory at Qualitative Analysis and Inorganic Preparations. Second Year Students work at Quantitative Analysis, and also take a Laboratory Course in Physics or some other subject. Third Year Students work in the "Schorlemmer" Laboratory of Organic Chemistry, and may also undertake experimental work in some special branch of Chemistry.

The Chemical Laboratories are open daily from 9.30 a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

Metallurgical Laboratory.—This has been recently much enlarged and re-equipped, mainly with a view to post-graduate work on the Structure of Metals and the Chemistry of Fuel.

Applied Organic Chemistry.—In connection with the "Schorlemmer" and "Schunck" Laboratories, a special laboratory is fitted with apparatus and appliances suitable for investigations on Dyes and other organic substances on a large scale.

Electro-chemical Laboratory.—In addition to such apparatus as is required for experimental work on Electrolysis and the Electro-deposition of Metals, special equipment is provided for investigations with the Electric Furnace.

Chemical Research.

In addition to the facilities mentioned above for Metallurgical and Electro-chemical Research, the following laboratories are available for post-graduate work:—(1) The Private Laboratories of the two Professors; (2) The "Frankland" Laboratories for Physical Chemistry; (3) The "Schunck" Laboratory for Organic Chemistry; (4) The "Thorpe" Laboratory for Organic Chemistry.

To encourage post-graduate work of this kind, the University gives a "Beyer" Fellowship (£100 per annum) and Scholarships (£25 or £50 per annum).

The "Dalton" Chemical Scholarship (£50 per annum, tenable for two years) is also awarded, and the 1851 Exhibition Scholarships (£150) may be held in the Laboratory. Further, Honorary Research Fellowships and Research Studentships are granted from time to time to those who are capable of carrying out original investigations.

Two "Schunck" Research Assistants are appointed annually, and it is proposed to establish a "Schunck" Fellowship.

Courses for Degrees.

To qualify for the Ordinary Degree of B.Sc. Students have to attend a prescribed course of study extending over three years, and are recommended to pass the Matriculation Examination before entrance. (Subsequent to October, 1906, three years attendance after matriculation will be compulsory).

The course of the Degree of B.Sc. with Honours in Chemistry is as follows:—First year: First year Honours Lectures; Mathematics (3 hours a week); Physics (3 hours a week); an additional course (3 hours a week); Chemical Laboratory (3 days per week). Second year: Second year Honours Lectures; General Organic Lectures; Physical or some other Laboratory (1 day per week); Chemical Laboratory (3 days per week). Third year: Third year Honours Lectures; Lecture course in some Special Branch of Chemistry; History of Chemistry; Chemical Laboratory (5 days per week, for one of which attendance in another Laboratory may be substituted).

For the M.Sc. Degree post-graduate work is required. The D.Sc. may be obtained after four years from graduation, provided that the candidate has distinguished himself in research.

Certificate in Applied Chemistry.—The course extends over three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

For further particulars of any of these courses apply to the Registrar, Edward Fiddes, M.A.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENTS OF CHEMISTRY AND METALLURGY.
Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—R. M. Caven, D.Sc., F.I.C.; G. Sand, Ph.D., M.Sc.; and R. E. Rose, Ph.D.

The Classes of the College are open to students of both sexes above sixteen years of age.

The Session commences on October 2nd, for both Day and Evening Classes.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Elementary Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

The fees for the Day Lectures and Classes are as follows: First year, two Lectures per week, 15s. per term. Second year, three Lectures per week, 22s. 6d. per term. Third year, four Lectures per week, 30s. per term.

Demonstrations and Lectures on Analytical Chemistry are given, and Chemical Calculation and Tutorial classes are also held. Various short courses of lectures on special subjects are delivered during the Session.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh; they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees for day students: For one term, £7; for the session, £18; for six hours weekly 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for two hours per week, three hours 15s., four hours 20s., per term.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students are provided with Lectures and Laboratory work suitable for the preparation for the Minor and Major Examinations.

Evening Classes.—Evening Lectures and Laboratory instruction will be given in Pure and Applied Chemistry, and the laboratories are open for practical work on Tuesday and Thursday evenings from 7 to 9. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

THE UNIVERSITY OF SHEFFIELD.

Professor of Chemistry—W. P. Wynne, D.Sc., F.R.S.

Lecturers and Demonstrators—A. N. Meldrum, D.Sc.; W. E. S. Turner, M.Sc., B.Sc.; W. J. Jarrard, B.Sc.

The Session will commence on October 4th.

Matriculation Course.—Tue-day and Friday at 9.30. Fee, £2 2s. 6d., and three hours per week Laboratory work.

Intermediate Course for B.Sc. or M.B.—Monday, Tuesday, Thursday, and Friday, at 9.30 a.m.; £3 13s. 6d., and nine hours per week Laboratory work.

B.Sc. Course.—Monday, Tuesday, and Friday, and another hour to be arranged, £5 15s. 6d., and twelve hours per week Laboratory work during two Sessions.

A Course of Lectures, with a special class in Laboratory Work, is arranged for Medical Students entering for the Conjoint Board Examinations.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.; Twenty-four, £14; Thirty-two, £17.

Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

A course of Elementary Practical Physics and Practical Chemistry, which will meet the requirements of candidates for the Diploma of Public Health will be held during the Michaelmas and Lent terms. Fee £5 5s.

An arrangement has been entered into with the Board of Education, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Board being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Evening Classes.—Lecture Class and Laboratory, on Wednesday evening. Sessional Fee, £1 10s. Fee for one term, 17s. 6d.

DEPARTMENT OF METALLURGY.

Professor of Metallurgy.—J. O. Arnold. This Department has been equipped to meet the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of Iron and Steel, Fuel, and Refractory materials. It also contains a complete pyrometric installation, and a laboratory for the study of the micrographic analysis of metals fully equipped with specially designed microscopes by Ross, polishing tables, etching appliances, incandescent light for evening work, &c. The School is now the most complete of its kind for teaching the practical manufacture, the chemical constitution, and the physical properties of Steel. Special attention is given to the determination of the microscopic constituents of Steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is not neglected, but is dealt with in a separate syllabus, dealing with metals (other than iron and steel) used in the arts. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates will be granted only to those who follow the prescribed courses, and pass the necessary examinations. Lectures on Iron and Steel Manufacture, on Fuel and Refractory Materials, and on General Metallurgy. Practical Metallurgy:—Laboratory, Furnaces, Foundry, and Testing Machine Course; Practical Course of Metallurgy other than Iron and Steel; Practical Fuel Course for Students engaged in Collieries or Gas-Works.

A new steel works has recently been erected in connection with the Sheffield College at a cost of about £10,000. The works include a two ton open-hearth furnace, a one ton Bessemer plant, and a four-hole crucible melting plant. The works are also provided with a hammer capable of dealing with four-inch ingots. Differential annealing furnaces, oil brightening and lead-tempering tanks will constitute part

of the new plant. Additional laboratory accommodation is attached to the works, viz., chemical laboratory for staff, chemical laboratory for post graduate students, together with a complete magnetic laboratory for hysteresis, &c.

UNIVERSITY COLLEGE, DUNDEE.

UNIVERSITY OF ST. ANDREWS.

Professor of Chemistry.—James Walker, Ph.D., D.Sc., F.R.S.

Assistant Lecturers.—J. S. Lumsden, Ph.D., D.Sc., and J. K. Wood, D.Sc.

Lecture Assistant and Laboratory Steward.—J. Foggie, F.C.S.

The Winter Session begins on October 16th, and ends on March 21st. The Summer Session extends from the middle of April to the end of June.

The *Junior Lecture Course on Systematic Chemistry* is given daily during the Winter Session, and embraces the Elements of Inorganic and of Organic Chemistry.

Advanced Courses, of about fifty lectures each, will be given during the year as follows:—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theoretical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. Special facilities are afforded to Research Students.

UNIVERSITY OF ABERDEEN.

CHEMISTRY.

Professor.—Francis R. Japp, M.A., LL.D., F.R.S.

Demonstrators.—Francis W. Gray, M.A., B.Sc., and John Alexander, M.A.

I. *General Lecture Course (100 Lectures).*—Daily during the Winter Session. The subjects treated of include (1) The Laws of Chemical Combination and the General Principles of Chemistry; (2) Non-metallic and Metallic Elements, and their Compounds; (3) Organic Chemistry; (4) Applications of Chemistry to the Arts and Manufactures. Fees, for first attendance, £4 4s.; for subsequent attendance, £3 3s. A Tutorial Class (without fee), conducted by the Junior Demonstrator, is held in connection with this course.

II. *Special Lecture Course on Organic Chemistry (50 Lectures).*—Daily during the Summer Session. Fee, £3 3s.

III. *Practical Course for Medical Students.*—This course, which occupies five hours a week during the Summer Session—in all fifty hours—is devoted to practice in Elementary Qualitative Analysis. Fee, £4 4s.

IV. *Chemical Laboratory.*—The Laboratory is open to Students daily from 9 a.m. to 5 p.m. Each Student on entering is allowed to arrange his hours of work so as to suit his own convenience, but must adhere to these hours when once fixed. The Laboratory instruction includes: (1) General experiments; (2) Preparations; (3) Qualitative analysis; (4) Quantitative analysis: gravimetric, volumetric, and gasometric. Fee, £4 4s. a session. A certain number of free places are available, on the recommendation of the Professor, and subject to the approval of the Senatus, for research students.

V. *Physical and Advanced Inorganic Chemistry (30 Lectures).*—In connection with the Laboratory work, three Lectures a week on Physical Chemistry and selected portions of Advanced Inorganic Chemistry are delivered during the Winter Session by the Lecturer, Mr. F. W. Gray. Fee, £2 2s.

UNIVERSITY OF ABERDEEN AND ABERDEEN AND NORTH OF SCOTLAND COLLEGE OF AGRICULTURE.

Agricultural Chemistry.

Lecturer.—James Hendrick, B.Sc., F.I.C.

Assistants.—R. Glegg, B.Sc., A.I.C., and W. J. Profeit, M.A., B.Sc.

I. Preparatory Courses in General Chemistry and in Organic Chemistry are given for those who are unable to

take the full University Courses in these subjects. The course in General Chemistry consists of about sixty Lectures with Practical Work (one hour daily) during the Winter Session. The course deals with the general principles of Chemistry, and with those parts of Inorganic Chemistry which are of more immediate concern to students of Agricultural Chemistry. The Practical Work goes along with and illustrates the Lectures. Fee, £4 4s.

The course in Organic Chemistry consists of about thirty Lectures, and is given during the Winter Session. It deals especially with those parts of the subject which are directly related to Agricultural Chemistry. Fee, £1 1s.

II. *Agricultural Chemistry (General Course).*—This class meets daily during the Winter Session, and includes both Lectures and Laboratory Work. The Lectures deal with the Chemistry of the Atmosphere, the Soil, Manures, Foods, Preservatives, Insecticides, &c. The Physiological Chemistry of Plants and Animals, the Composition and Manurial Requirements of Crops, and Dairy Chemistry are also treated of. The Laboratory Work is primarily intended to accompany and illustrate the Lectures. Exercises dealing with the properties and composition of Soils, Manures, Feeding-stuffs and Waters, and with the impurities and adulterations of these, occupy much of the time given to Practical Work. The fee for the whole Course (Lectures and Practical Work) is £4 4s.

III. *Laboratory.*—A Summer Course in Practical Chemistry is given to prepare students who have not previously done sufficient laboratory work for the course in Agricultural Chemistry. Fee, £2 2s.

IV. The Laboratory is open daily from 9 a.m. to 5 p.m. for students who wish to study the principles and practice of Agricultural Chemistry or to undertake research in this subject.

UNIVERSITY OF EDINBURGH.

DEPARTMENT OF CHEMISTRY.

Professor—Alex. Crum Brown, M.D., D.Sc., F.R.S.

Lecturers—L. Dobbin, Ph.D.; H. Marshall, D.Sc.; and W. W. Taylor, M.A., D.Sc.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to middle of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee £4 4s. An Advanced Course of twenty-five lectures is also given in the Winter Session; fee, £2 2s. An Intermediate Course of Organic and Advanced Inorganic Chemistry is held in summer; fee, £2 2s. There is also a class on History of Chemistry or Chemical Theory, by Dr. Dobbin; fee £1 1s.; and a class on Mineralogy and Crystallography, by Dr. Marshall; fee, £2 2s. All these Lectures, except the General Course, are now open to women.

In addition to the above, Lecture Courses are from time to time given by the Assistants on particular branches of Organic and Inorganic Chemistry. These Lectures are free to Laboratory Students.

Laboratories.—Practical classes for Medical Students meet during the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for Science and Arts Students engaged in analytical and advanced practical work are open daily from 9.30 till 4.30. (Fees: Whole Day—Winter Session, £10 10s.; Oct.-Dec., Jan.-March, or Summer Session, £5 5s. Half Day—Winter Session, £6 6s.; Oct.-Dec., Jan.-March, or Summer Session, £3 3s. Preference will be given to students in the above order. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry (including Gas Analysis), Physico-chemical Measurements, Agricultural Chemistry, and Assaying. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical language, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination in Pure Science includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy (including Anthropology), Physiology, Geology (including Mineralogy), Zoology (including Comparative Anatomy), and Botany (including Vegetable Physiology). In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic, including Mineralogical, Chemistry; Organic Chemistry; Chemical Crystallography; History of Chemistry. In the written papers a choice of questions is allowed, so as to adapt the examination to the various courses of advanced study which candidates may have selected. Practical Examination:—Complex Qualitative Analysis; Inorganic Preparations; Gravimetric and Volumetric Analysis. Each candidate taking the higher standard will also be examined on Organic Preparations, Ultimate Organic Analysis, and one of the following subjects, selected by himself:—Gas Analysis; Assaying; Physico-chemical Measurements.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. Laurie, M.A., D.Sc., F.R.S.E.

Professor—John Gibson, Ph.D., F.R.S.E.

Assisted by the following Lecturers and Demonstrators:—Bertie M. Steele, D.Sc.; Archibald Boon, B.A., B.Sc.; Andrew F. King, F.I.C.; and Dr. Emil Westergaard.

The Session begins October 3th, 1905.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Chemistry Course is designed to meet the wants of Manufacturing Chemists. The instruction consists of Courses in Chemistry, Physics, Mathematics, Engineering, and Mechanical Drawing, with Special Courses in Gas and Paper Manufacture, Brewing, &c., by Experts, in the fourth year. Special attention will be paid to Electro-chemistry. The Chemistry Classes are recognised by the University as qualifying for the B.Sc., in Chemistry, and are also recognised by the Institute of Chemistry.

For Chemistry Students in the fourth year arrangements have been made for their spending twelve months in the laboratories of the Corporation's Gas Works, with a view to the study of problems connected with the Combustion of Fuel, the Manufacture of Coal-gas and its By-products, &c.

A Laboratory has been provided for the study of Micro-

organisms in connection with Brewing, Distilling, Vinegar Making, Tanning, Preserving, Starch and Sugar Making, Butter and Cheese Manufacture.

Matriculation Fee, 5s.; Composition Fee for Engineering Courses, £12 12s. per Session; for Chemistry Courses, First Session, £12 12s.; Second Session, £12 12s.; Third Session, £15 15s.; Fourth Session, £15 15s. Full particulars are published in the Calendar of the College early in September.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A.
Professor of Technical Chemistry—T. Gray, D.Sc., Ph.D.
Professor of Metallurgy—A. Humboldt Sexton, F.C.S., F.R.S.E.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

Session opens Sept. 26. Entrance Examination Sept. 18. The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1905-1906 may be had from Mr. H. F. Stockdale, Secretary; price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS. UNITED COLLEGE OF ST. LEONARD AND ST. SALVATOR.

Professor of Chemistry—T. Purdie, B.Sc., Ph.D., LL.D., F.R.S.

The Session begins on October 13th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for forty Bursaries, ranging in value from £40 to £10 each per annum, will be held on September 29th and following days. Twenty-five of these Bursaries are restricted to Men, one to Men and Women, and fourteen to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine.

A Hall of Residence is provided for Women Students.

Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only

cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment.

This course of instruction is intended to meet the requirements of the M.A., First Science, and M.B., Ch.B. Exams., so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part to General and Physical Chemistry, the instruction in general being such as is required for the Final Science Exam.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £4 4s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Original Investigation. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the Examinations in Arts, Science, and Medicine.

The fee for the Ordinary Course of Practical Chemistry is £3 3s. and for the Advanced Course £5 5s.

QUEEN'S COLLEGE, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.U.I., F.R.S.E., &c.

I.—Chemistry.—The lectures are delivered at 3 p.m., on the first five days of each week, and terminate at the end of March. The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry. Fee, £2.

II.—Practical Chemistry.—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3.

III.—Laboratory Pupils.—The Chemical Laboratory is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

The new Chemical Laboratories are now open, and are provided with all modern appliances. Special facilities are offered to those engaged in Research work.

Scholarships.—The following College Scholarships are awarded specially in connection with the schools of Chemistry and Physics:—Senior Scholarships in Chemistry alone awarded annually of £40, and tenable for one year. Andrews Studentship in Chemistry and Physics, value about £80 annually, and tenable for two years. 1851 Exhibition Scholarships: One of these Scholarships has hitherto been placed at the disposal of the College every two years, of the annual value of £150, tenable for two or under special conditions for three years.

The following Scholarships, &c., of the Royal University of Ireland are awarded in the same group of subjects (Chemistry and Physics):—At the B.A. Degree examination, First-class Exhibitions of £42 each and Second-class Exhibitions of £21. At the M.A. Degree examination, a Studentship of £100 per annum, tenable for three consecutive years. Also a Junior Fellowship, tenable for four years, of the annual value of £200.

QUEEN'S COLLEGE, CORK.

Professor—Augustus Edward Dixon, M.D.

Demonstrator—John Hawthorne, Ph.D., F.C.S.

The College Session will commence on October 17th,

1905, and end on June 9th, 1906. All classes are open to male and female students.

The courses in Chemistry, though designed primarily to meet the requirements of candidates proceeding to the Examinations in Arts, Medicine, and Engineering of the Royal University of Ireland, of the Medical Licensing Bodies of Dublin and Edinburgh, and of the Pharmaceutical Society of Ireland, can be specially arranged as required, so as to render them suitable to any particular course of study. The following courses are provided:—

Systematic Chemistry.

I. General Lecture Course; three terms. Inorganic Chemistry, Elementary Organic Chemistry, and Chemical Philosophy.

II. Advanced Organic Chemistry, and Chemical Philosophy.

Practical Chemistry.

III. Winter Course of Practical Analytical Chemistry; commencing early in January, 1906.

IV. Summer Course of three months' duration, for students of Medicine; ending about the third week in June.

V. Course for Pharmaceutical Students; held during the second and third terms.

Laboratory Work.

VI. The Chemical Laboratory is open daily from 10 to 4 o'clock, to Students entering for Special Courses of practical work in General Inorganic Chemistry, Qualitative and Quantitative Analysis, Organic Chemistry, or for the purpose of Original Investigation.

Scholarships, &c.—In addition to the Class Prizes given at the Sessional Examinations, the College awards a Senior Scholarship of the value of £40, for Chemistry and Physics (either of which may be taken as a limited course), and numerous Junior Scholarships in Arts, Medicine, and Engineering, of which chemistry forms a part, value from £20 to £24 each, annually. The Royal University of Ireland also offers Exhibitions in Chemistry and Physics, First-class value £42, and Second-class value £21, together with other prizes, e.g., a Studentship of £100 per annum, tenable for three years; and the 1851 Exhibition Scholarships, value £150, tenable for two, and, under certain circumstances, for three years, have from time to time been placed at the disposal of the College.

Full particulars as to Lectures, Fees, Scholarships, Exhibitions, &c., are contained in the Regulations extracted from the College Calendar, which will be supplied on application to the Registrar.

QUEEN'S COLLEGE, GALWAY.

Professor—Alfred Senior, Ph.D., M.D., F.I.C., F.C.S.

Demonstrator—Miss Rosalind Clarke, B.A.

Research Assistants—W. Sloan Mills, M.A., and Percy C. Austin, M.A.

The College Session commences in October and ends in June.

Chemistry is studied by attendance at Lectures, by work in the Laboratories, and by the use of the College Library. The Courses in the several faculties are arranged with a view to the requirements of the Royal University of Ireland, but are adapted also to those of other Universities and licensing bodies.

Lecture Courses. Faculty of Arts.—1. Second year's Course, Inorganic and the Elements of General Chemistry. 2. Third year's Course, Advanced Organic Chemistry. 3. Fourth year's Post-Graduate Course, Advanced General Inorganic and Organic Chemistry. *Faculty of Medicine.*—First year's Course, Inorganic and Elementary Organic Chemistry. *School of Engineering.*—First year's Course, Inorganic Chemistry.

Laboratory Courses. Faculty of Arts.—1. Second year's Course, Exercises in Inorganic Qualitative Analysis. 2. Third year's Course, Quantitative Analysis and other experiments to suit the requirements of individual Students. 3. Fourth year's Post-Graduate Course, Advanced Quantitative Analysis, Organic and Inorganic Prepara-

tions, and determination of their Physical and Chemical characters. 4. The Laboratories are also open to Students for work in other branches of Chemistry. *Faculty of Medicine.*—1. Second year's Course, Inorganic and Organic Elementary Qualitative Analysis, and the Chemical Examination of Urine. *School of Engineering.*—1. Second year's Course, Inorganic Qualitative Analysis.

A Scholarship in Chemistry is offered for competition each year of the value of £40, and Chemistry enters into the subjects required for numerous Scholarships in Arts, Medicine, and Engineering. The Royal Commissioners for the Exhibition of 1851 offer every two years a Science Research Scholarship of £150 per annum. This Scholarship has already been held by four Chemistry Students of this College.

For details as to Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar, published in December, and the Extracts from Calendar, published in advance in July, may be obtained.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

Dean of Faculty and Professor of Chemistry—W. N. Hartley, F.R.S., D.Sc.

Lecturer on Organic Chemistry—Alphonsus O'Farrelly, M.A.

Senior Assistant—J. Holms Pollok, D.Sc.

The Royal College of Science supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Engineering (Mechanical and Electrical), Applied Chemistry, and Agriculture. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Applied Chemistry is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Organic Chemistry, Elementary and Advanced; (3) Analytical and Experimental Chemistry; (4) Instruction in Chemical Research.

Fees payable by Non-Associate Students:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months. £12 for the entire session.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College.

A limited number of Scholarships in Science and Technology are competed for each year. These Scholarships include free education for the full Associateship Course of three years and maintenance allowance of a guinea a week during the Session.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. The Programme

of the College, containing full particulars of the conditions of entrance, fees, and courses of instruction, may be had on application. *City and Guilds Technical College, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations begin on Tuesday, September 19th, and the Winter Session opens on Tuesday, October 3rd. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College on Tuesday, September 19th. Session begins October 3rd. *South London Technical Art School.*—Classes in Modelling, Design, Drawing and Painting, House Decoration.

CITY OF LONDON COLLEGE, White Street, Moorfields.—I. S. Scarf, F.I.C., F.C.S., and Assistants. Courses of Evening Lectures and Laboratory Practice in Chemistry and Physics, open to Students of both sexes. Day Commercial School, commences Sept. 18. Session commences October 2.

BATTERSEA POLYTECHNIC.—Principal, Mr. Sidney H. Wells, Wh.Sc. Inorganic, Organic, and Technological Chemistry, Mr. John Wilson, M.Sc. (Vit.), assisted by Mr. John L. White, D.Sc., Mr. H. Evans, and others. Session opens Sept. 25. Complete courses of instruction are given in Chemistry (Inorganic and Organic), together with Physics, Electricity, Engineering subjects, German, &c., for intending technological and works chemists. Certain of the Courses (Day and Evening) are recognised by the University of London in preparation for the B.Sc., for which examination (Pass and Honours) complete courses of instruction, under recognised teachers, are provided. Special Evening Courses in Paper Testing, Paper Making, Gas Analysis, Oils, Fats, and Soaps, Chemistry of Building Materials, Chemistry of Foods, &c.

BIRKBECK COLLEGE, Breams Buildings, Chancery Lane.—Chemistry Courses conducted by Dr. J. E. Mackenzie prepare for various Examinations, the B.Sc. and M.B. Degrees of the London University, Conjoint Board, Pharmaceutical Examinations, Board of Education, &c. This Institution, which has now completed eighty-two years of educational work, will commence the new Session on Monday, October 2, when the Right Hon. Sir Edward Fry will give the Opening Address, at 7.30 p.m. The

Day and Evening courses of study comprise the various branches of Natural Science (Chemistry, Physics, Botany, Zoology, Geology, &c.), Mathematics, Latin, Greek, Modern Languages, Economics, Law, Logic, and Commercial Subjects. Courses conducted by recognised teachers of the University provide for the Examinations of the University of London, in the faculties of Arts, Science, Commerce, and Law. The Report for the last session shows that during the year 84 students passed some University examinations, while a large number gained successes at various public examinations. The College has added considerably to its appliances in recent years, and the Physical, Chemical, Biological, and Metallurgical laboratories are very thoroughly equipped. Courses in Mining, Metallurgy, and Assaying are given both in the day and evening. The Modern Language classes include Italian, Spanish, and Russian, as well as French and German. The College has a School of Art, open both day and evening. Good Reading and Magazine Rooms are provided. The Calendar supplies detailed information respecting the Courses of Study, Examinations, Studentships, &c. A popular Lecture or Entertainment is given in the Theatre every Wednesday evening from October to May.

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Honours Examination and research. Evening Classes for London University Degrees are also held. The Day College opens on Sept. 18. Evening Classes begin Sept. 25.

UNIVERSITY TUTORIAL COLLEGE, 32, Red Lion Square, Holborn, W.C.—This Institution contains large Laboratories for Chemistry, Physics, Geology, and other subjects. Classes are specialised for Examinations of London University, but students may take up work for any Examination. The special feature of the College is that work goes on all the year round, thus affording students residing in the Country an opportunity of doing practical work during their Vacations.

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in a University recognised by the Council, is eligible for admission to the Intermediate Examination of the Institute. Holders of certain Degrees or Diplomas are exempt from passing the Intermediate, and, by virtue of their qualifications, are eligible for admission to the Final Examination direct. *The Final Examination for the Associateship (A.I.C.)*.—Any Candidate who has passed the Intermediate Examination of the Institute, or who is entitled to claim exemption from passing the Intermediate Examination, is eligible for admission to the Final Examination. *Fellowship (F.I.C.)*.—For admission to the Fellowship, an Associate is required to have been registered for three years, and to have been continuously engaged during that period in the study and practical work of Applied Chemistry in a manner satisfactory to the Council. Full particulars are given in "The Book of Regulations for the Admission of Students, Associates, and Fellows," which may be obtained on application to Messrs. Blundell, Taylor, and Co., 773, Upper Thames Street, London, E.C. Price One Shilling.

BLACKBURN MUNICIPAL TECHNICAL SCHOOL.—Chemistry: Mr. Robert H. Pickard, D.Sc. (Lond.), &c., assisted by Messrs. Jos. Yates, W. O. Littlebury, and H. L. Leech. Session opens Monday, September 11. Full details of the Classes are given in the "Students' Handbook," which may be had at the Institution (price 1d., by post 2½d.).

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the teaching of Chemistry, as might be expected in a district where the Chemical industries are important, is of an exceptionally complete character. It comprises, in addition to ample accommodation for pure Chemistry, laboratories for Metallurgy, Brewing, Bleaching, Dyeing and Printing, Paper-making, and Electro-chemistry. The Bleaching, Dyeing, Printing and Finishing, and the Paper-making industries are in addition extensively equipped in a separate building with machinery and appliances on an industrial scale. A Brew-house is also equipped on the low gravity principle, with a plant of four bushel capacity.

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THE CHEMICAL NEWS.

VOL. XCII., No. 2397.

DIAMONDS.

A LECTURE DELIVERED BEFORE THE BRITISH ASSOCIATION
AT KIMBERLEY, SEPTEMBER 5, 1905.

By Sir WILLIAM CROOKES,
Hon. D.Sc. (Oxford and Dublin), F.R.S.

If ever a man felt the real inwardness of the saying, "Carrying coals to Newcastle," it is I, who audaciously stand before you this evening. My difficulties are threefold. I have to address an audience thickly sprinkled with experts on a subject in which I am a mere graduate. I also have to address Members of the British Association, and if possible interest them in the wonderful development of an Industry which has made the few square miles in the centre of which we are standing the most valuable land on the face of the earth; and likewise I wish to illustrate the various properties of the diamond in a series of experiments few of which can be rehearsed beforehand,—as experiments sometimes destroy the stones,—and diamonds, as probably some present are aware, are expensive playthings.

From the earliest times the diamond has fascinated mankind. It has been a perennial puzzle—one of the "riddles of the painful earth." It is recorded in "Sprat's History of the Royal Society" (1667) that among the questions sent by order of the Society to Sir Philiberto Vernatti, Resident in Batavia, was one inquiring "Whether Diamonds grow again after three or four years in the same places where they have been digged out?" The answer sent back was "Never, Or at least as the memory of man can attain to."

In a lecture "On Diamonds," more than forty years ago Professor Maskelyne said (CHEMICAL NEWS, vol. i., p. 208):—"The diamond is a substance which transcends all others in certain properties to which it is indebted for its usefulness in the arts and its beauty as an ornament. Thus, on the one hand it is the hardest substance found in nature or fashioned by art. Its reflecting power, and refractive energy, on the other hand, exceed those of all other colourless bodies, while it yields to none in the perfection of its pellucidity." He was constrained to add "The formation of the diamond is an unsolved problem."

Of late years the subject has fascinated many men of science. The development of electricity, with the introduction of the electric furnace, has facilitated research, and I am justified in saying that if the diamond problem is not actually solved, there is every probability it shortly will be solved.

South Africa, as I will show in detail, is the favourite haunt of diamonds on this planet; it ranks with Australia and California as one of the three great gold-yielding regions. But the wealth of South Africa is not limited to gold and diamonds. It is also the illimitable home of Coal—"the Black Diamond of the Universe." The province of Natal alone contains more coal than Britain ever owned before a single bucket had been raised; and the coal beds extend into the Orange River Colony. Valuable iron ores exist also in large quantities.

In addition to these lavish natural riches the high grounds above Cape Town abound in medicinal health-giving waters. The districts where these springs occur are high lying, free from malaria, and admirably adapted for the restoration of invalids. It needs only some distinguished individual to set the fashion, some Emperor, Prince, or reigning Beauty to take the baths and drink the waters, and the tide of tourists will surely carry prosperity to Aliwal North, Fraserburg, Cradock, and Fort Beaufort.

It is to the Diamond industry I specially direct your attention to-night. I have studied diamonds scientifically for thirty years, and of the Kimberley mines I speak with the freshness of personal experience. In 1896 I spent nearly a month at Kimberley, when Mr. Gardner Williams, General Manager of the De Beers Consolidated Mines, and the Managers of neighbouring mines, did their utmost to assist me in my enquiries and to aid me with valuable information. I had free access to all the workings, above and below ground, examined at leisure their stock and took extracts from their books. I had exceptional opportunities of studying the peculiar geological formation, and of noting facts connected with the birth of the precious stone which forms the subject of this evening's lecture.

Although my experiments are chiefly connected with the physical and chemical properties of diamonds, and with researches on the perplexities of their probable formation, it will be a kind of compensation for the dryness of some theoretical points, if with the help of a few photographs—taken on my former visit to South Africa—I bring before your eyes the general character of the mines and their surroundings.

The most famous diamond mines are Kimberley, De Beers, Dutoitspan, Bultfontein, and Wesselson. Kimberley is practically in the centre of the present diamond-producing area. The mines are situated in latitude $28^{\circ} 43'$ South, and longitude $24^{\circ} 46'$ East. There are also River Washings in the neighbourhood of the Vaal river, where the work is conducted in somewhat primitive fashion. When I was at Klipdam, miners had congregated at a spot called "New Rush," where some good finds of diamonds had been reported. At one of the claims where work was proceeding vigorously I asked the proprietor to let me be present at the sorting out. He willingly consented, but no diamonds were found. On my expressing regret, he said he had not seen a diamond for a fortnight! but then he had picked out one worth £300, "and that," he said, "will pay for several weeks' wages of my boys." This is the kind of speculative gambling that goes on at the river diggings. The miner may toil fruitlessly for months, and then luckily come across a pocket of stones, swept there by some eddy, by which he will net thousands. Diamonds from the "river washings" are of all kinds, as if contributed by every mine in the neighbourhood. They are much rolled and etched, and contain a fair proportion of stones of good quality, as if only the better and larger diamonds had survived the ordeal of knocking about. Besides these mines, there are in the Orange River Colony—about 60 miles from the Kimberley diamond region—two others of some importance known as Jagersfontein and Koffyfontein, whilst about 20 miles W.N.W. of Pretoria is situated the New Premier mine, now famous as the home of the wonderful "Cullinan" diamond.

Kimberley.

The surface of the country round Kimberley is covered with a ferruginous red, adhesive, sandy soil, which makes traffic heavy. Below the red soil is a basalt, much decomposed and highly ferruginous, from 20 to 90 feet thick, and lower still from 200 to 250 feet of black slaty shale containing carbon and iron pyrites. Then deeper a bed of conglomerate about 10 feet thick, and below the conglomerate about 400 feet of a hard compact rock of an olive colour, called "Melaphyre," or Olivine diabase. Below the melaphyre is a hard quartzite about 400 feet thick. The strata are almost horizontal, dipping slightly to the north; in places they are distorted and broken through by protruding dykes of trap. There is no water nearer than the Vaal river, about 14 miles away; formerly the miners were dependent on rain-water and a few springs and pools. Now, however, a constant and abundant supply of excellent water is served to the town. Good brick houses, with gardens and orchards, have sprung up on all sides.

* "MELAPHYRE. A waiting room for Rocks, till called for.

The Pipes.

The five diamond mines are all contained in a precious circle 3½ miles in diameter. They are irregular shaped round or oval pipes, extending vertically downwards to unknown depths, retaining about the same diameter throughout. They are considered to be volcanic necks, filled from below with a heterogeneous mixture of fragments of surrounding rocks, and of older rocks such as granite, mingled and cemented with a bluish coloured hard clayey mass, in which famous blue clay the imbedded diamonds are hidden.

The areas of the mines are:—

Kimberley	33 acres
De Beers	22 „
Dutoitspan	45 „
Bultfontein	36 „

Before the discovery of the mines there was nothing in the superficial appearance of the ground to indicate the priceless treasures below. Since the filling of the volcanic ducts with diamantiferous ground, denudation has planed the surface; and the upper parts of the craters and other ordinary signs of volcanic activity being smoothed away, the superficial and ubiquitous red sand has covered and disguised the whole surface. The Kimberley mine seems to have presented a slight elevation above the surrounding flat country, while the sites of other mines were level or even slightly depressed.

Other diamantiferous pipes in the neighbourhood are small and do not contain stones in payable quantities. Hoards of diamonds may await the lucky discoverer, but where there are no surface signs, and the pipe itself is hidden under 10 or 20 feet of recent deposits, prospecting is a matter of sheer speculation. Hitherto accident has been the chief factor in the discovery of diamond mines.

How the great pipes were originally formed is hard to say. They were certainly not burst through in the ordinary manner of volcanic eruption, since the surrounding and enclosing walls show no signs of igneous action, and are not shattered or broken up even when touching the "blue ground." It is pretty certain these pipes were filled from below after they were pierced, and the diamonds were formed at some previous time and mixed with a mud volcano, together with all kinds of *débris* eroded from the rocks through which it erupted, forming a geological "plum pudding." The direction of flow is seen in the upturned edges of some of the strata of shale in the walls, although I was unable to see any upturning in most parts of the walls of the De Beers mine at great depths.

The breccia filling the mines, usually called "blue ground," is a collection of fragments of shale, and of various eruptive rocks, boulders, and crystals of many kinds of minerals. Indeed, a more wildly heterogeneous mixture can hardly be found anywhere else on this globe. The Kimberley mines for the first 70 or 80 feet are filled with so-called "yellow ground," and below that with "blue ground." This superposed yellow on blue is common to all the mines. The blue is the aboriginal ground, and owes its colour chiefly to the presence of lower oxides of iron. When atmospheric influences have access to the iron it becomes peroxidised, and the ground assumes a yellow colour. The thickness of yellow earth in the mines is therefore a measure of the depth of penetration of air and moisture. The colour does not affect the yield of diamonds. The ground mass is soapy to the touch, and friable, especially after exposure to weather. Besides diamonds, more than eighty species of minerals have been recognised in the blue ground, the most common being—Magnetite, ilmenite, garnet, bright green ferriferous enstatite (bronzite), a hornblende mineral closely resembling smaragdite, calc-spar, vermiculite, diallage, jeffreysite, mica, kyanite, augite, peridot, iron pyrites, wollastonite, vaalite, zircon, chrome iron, rutile, corundum, apatite, olivine, sahlite, chromite, pseudobrookite, perovskite, biotite, and quartz.

The blue ground does not show any signs of igneous action; the fragments in the breccia are not fused at the

edges. The eruptive force was probably steam or water-gas, acting under great pressure but at no high temperature.

There are many such pipes in the immediate neighbourhood of Kimberley. It may be that each volcanic pipe is the vent for its own special laboratory—a laboratory buried at vastly greater depths than we have yet reached—where the temperature is comparable with that of the electric furnace, where the pressure is fiercer than in our puny laboratories and the melting-point higher, where no oxygen is present, and where masses of liquid carbon have taken centuries, perhaps thousands of years, to cool to the solidifying point. The chemist arduously manufactures infinitesimal diamonds, valueless as ornamental gems; but Nature, with unlimited temperature, inconceivable pressure, and gigantic material, to say nothing of measureless time and appalling energy, produces without stint the dazzling, radiant, beautiful, coveted crystals I am enabled to show you to-night.

This hypothesis of the origin of diamonds is in many ways corroborated.

The ash left after burning a diamond invariably contains iron as its chief constituent; and the most common colours of diamonds, when not perfectly pellucid, show various shades of brown and yellow, from the palest "off colour" to almost black. They are also green, blue, pink, yellow, and orange. These variations give support to the theory advanced by Moissan that the diamond has separated from molten iron,—a theory of which I shall say more presently,—and also explain how it happens that stones from different mines, and even from different parts of the same mine, differ from each other. Further confirmation is given by the fact that the country round Kimberley is remarkable for its ferruginous character, and iron-saturated soil is popularly regarded as one of the indications of the near presence of diamonds. Along with carbon, molten iron dissolves other bodies which possess tinctorial powers. One batch of iron might contain an impurity colouring the stones blue, another lot would tend towards the formation of pink stones, another of green, and so on. Cobalt, nickel, chromium, and manganese, all metals present in the blue ground, would produce these colours.

An hypothesis, however, is of little value if it only elucidates half a problem. Let us see how far we can follow out the ferric hypothesis to explain the volcanic pipes. In the first place we must remember these so-called volcanic vents are admittedly not filled with the eruptive rocks, scoriaceous fragments, &c., constituting the ordinary contents of volcanic ducts.

A selection of thin sections of some of these rocks and minerals, mounted as microscopic objects and viewed by polarised light, are not only of interest to the geologist, but are objects of great beauty.

The appearance of shale and fragments of other rocks testify that the mélange has suffered no great heat in its present condition, and that it has been erupted from great depths by the agency of water vapour or some similar gas. How is this to be explained?

You will recollect I start with the reasonable supposition that at a sufficient depth* there were masses of molten iron at great pressure and high temperature, holding carbon in solution, ready to crystallise out on cooling. Far back in time the cooling from above caused cracks in superjacent strata through which water† found its way. On reaching the incandescent iron, the water would be converted into gas, and this gas would rapidly disintegrate and erode the channels through which it passed, grooving a passage more and more vertical in the necessity to find the quickest vent to the surface. But steam in the presence of molten or even red-hot iron liberates large volumes of hydrogen gas, together with less quantities of hydrocarbons;‡ of all

* A pressure of fifteen tons on the square inch would exist not many miles beneath the surface of the earth.

† There are abundant signs that a considerable portion of this part of Africa was once under water, and a fresh water shell has been found in apparently undisturbed blue ground at Kimberley.

‡ The water sunk in wells close to the Kimberley mine is sometimes impregnated with paraffin, and Sir H. Roscoe extracted a solid hydrocarbon from the "blue ground."

kinds—liquid, gaseous, and solid. Erosion commenced by steam would be continued by the other gases; it would be easy for pipes, large as any found in South Africa, to be scored out in this manner.

Sir Andrew Noble has shown that when the screw stopper of his steel cylinders in which gunpowder explodes under pressure is not absolutely perfect, gas escapes with a rush so overpowering as to score a wide channel in the metal. Some of these stoppers and vents are on the table. To illustrate my argument Sir Andrew Noble has been kind enough to try a special experiment. Through a cylinder of granite is drilled a hole 0.2 inch diameter the size of a small vent. This is made the stopper of an explosion chamber, in which a quantity of cordite is fired, the gases escaping through the granite vent. The pressure is about 1500 atmospheres, and the whole time of escape is less than half a second. Notice the erosion produced by the escaping gases and by the heat of friction; these forces have scored out a channel more than half an inch diameter and melted the granite along their course. If steel and granite are thus vulnerable at comparatively moderate gaseous pressure, it is easy to imagine the destructive upburst of hydrogen and water-gas grooving for itself a channel in the diabase and quartzite, tearing fragments from resisting rocks, covering the country with *débris*, and finally, at the subsidence of the great rush, filling the self-made pipe with a water-borne magma in which rocks, minerals, iron oxide, shale, petroleum, and diamonds are violently churned in a veritable witch's cauldron! As the heat abated the water vapour would gradually give place to hot water, which forced through the magma would change some of the mineral fragments into the existing forms of to-day.

Each outbreak would form a dome-shaped hill; the eroding agency of water and ice would plane these eminences until all traces of the original pipes were lost.

Actions such as I have described need not have taken place simultaneously. As there must have been many molten masses of iron with variable contents of carbon, different kinds of colouring matter, solidifying with varying degrees of rapidity, and coming in contact with water at intervals throughout long periods of geological time—so must there have been many outbursts and upheavals, giving rise to pipes containing diamonds. And these diamonds by sparseness of distribution, crystalline character, difference of tint, purity of colour, varying hardness, brittleness, and state of tension, have the story of their origin impressed upon them, engraved by natural forces,—a story which future generations of scientific men may be able to interpret with greater precision than is possible to-day.

The contents of the several pipes are not absolutely identical. The diamonds from each pipe differ in character, showing that the upflow was not simultaneous from one large reservoir below, but the result of several independent eruptions. Even in the same mine there are visible traces of more than one eruption.

The blue ground varies in its yield of diamonds in different mines.

According to tables furnished by the De Beers Company, the yield of the De Beers and Kimberley mines has declined as the depth increases. At the same time the value of the stones has risen, and diamonds are more expensive to-day than at any previous time. (See Table, next column).

The diamonds from each mine have a distinctive character, and so uniform are the characteristics that an experienced buyer can tell at once the locality of any particular parcel of stones. De Beers and Kimberley mines are distinguished by the yield of large yellowish crystals with curved edges; Dutoitspan yields mainly coloured stones, while Bultfontein—half a mile off—produces small white octahedral crystals, occasionally speckled and flawed, but rarely coloured. The diamonds from the Wesselson mine are characterised by the large number of perfect octahedra of pure water amongst them. The diamonds from the Leicester mine have a frosted, etched appearance; they are white, the crystallisation irregular ("cross-grained"), and they are hard and expensive to cut. Stones from Jagersfontein, in the Orange River

Year.	Number of carats* per load.†	Value per carat.	
		s.	d.
1889	1.283	19	8.75
1890	1.15	32	6.75
1891	0.99	29	6
1892	0.92	25	6
1893	1.05	29	0.6
1894	0.89	24	5.2
1895	0.85	25	6
1896	0.91	26	9.4
1897	0.92	26	10.6
1898	0.80	26	6.2
1899	0.71	29	7.2
1900	0.67	35	10.2
1901	0.76	39	7
1902	0.76	46	5.7
1903	0.61	48	6.3
1904	0.54	48	11.8

* According to Gardner Williams the South African carat is equivalent to 3.174 grains. In Latimer Clark's "Dictionary of Metric and other Useful Measures," the diamond carat is given as equal to 3.1683 grains = 0.2053 gramme = 4 diamond grains. One diamond grain = 0.792 troy grain. 151.5 diamond carats = 1 ounce troy.

Webster's "International Dictionary" gives the diamond carat as equal to 3.15th troy grains.

"The Oxford English Dictionary" says the carat was originally 1/144th of an ounce, or 3 1/3rd grains, but now equal to about 3 1/5th grains, though varying slightly with time and place.

"The Century Dictionary" says the diamond carat is equal to about 3 1/6th troy grains, and adds, that in 1877 the weight of the carat was fixed by a syndicate of London, Paris, and Amsterdam jewellers at 205 milligrammes. This would make the carat equal to 3.163 troy grains.

† A load weighs about 1600 lbs.

Colony, display great purity of colour and brilliancy and they have the so-called "steely" lustre characteristic of old Indian gems.

Let me cite a description of a visit to Kimberley in 1872, by Mr. Paterson, who gives a graphic picture of the early days.

"The New Rush Diggings (as the Kimberley mine was first called) are all going forward in an oval space enclosed around by the trap dyke, of which the larger diameter is about 1000 feet, while the shorter is not more than 700 feet in length. Here all the claims of 31 feet square each are marked out with roadways about 12 feet in width, occurring every 60 feet. Upon these roadways, beside a short pole fixed into the roadway, sits the owner of the claim with watchful eye upon the Kafir diggers below, who fill, and hoist by means of a pulley fixed to the pole above, bucketful after bucketful of the picked marl stuff in which the diamonds occur."

Soon came the difficulty how to continue working the host of separate claims without infringements. A system of rope haulage was then adopted. This mode of haulage continued in vogue during the whole of 1873, and if the appearance of the mine was less picturesque than when roadways existed, at least by moonlight it was a weird and beautiful sight.

But the mine was now threatened in two other quarters. The removal of the blue ground undermined the support from the walls of the pipe, and frequent falls of reef occurred, not only burying valuable claims but endangering the lives of workers below. Moreover, as the workings deepened, water made its appearance, necessitating pumping.

It soon became evident that open workings were doomed, and by degrees was devised the present system of underground working.

During this time of perplexity, individual miners who might have managed one or two claims near the surface could not continue work in the face of harassing difficulties and heavy expenses. Thus the claims gradually changed hands until the mine became the property first of a comparatively small number of capitalists, then of a smaller number of limited liability companies, until the whole of the mines have practically become the property of the "De Beers Consolidated Mines, Limited."

Underground Workings.

In the face of constant developments I can only describe the system in use at the time of my own visit—1896. Shafts are sunk in the solid rock at a sufficient distance from the pipe to be safe against reef movements in the open mine. In 1903, the rock shafts in the De Beers and Kimberley mines reached depths of 2076 and 2599 feet respectively. Tunnels are driven from these shafts at different levels, about 120 feet apart, to cross the mine from west to east. These tunnels are connected by two other tunnels running north and south, one near the west side of the mine and one midway between it and the east margin of the mine. From the east and west tunnels, offsets are driven to the surrounding rock. When near the rock, the offsets widen into galleries, these in turn being stoped on the sides until they meet, and upwards until they break through the blue ground. The fallen reef with which the upper part of the mine is filled sinks and partially fills the open space. The workmen then stand on the fallen reef and drill the blue ground overhead, and as the roof is blasted back the *débris* follows. When stoping between two tunnels the blue is stoped up to the *débris* about midway between the two tunnels. The upper levels are worked back in advance of the lower levels, and the works assume the shape of irregular terraces. The main levels are from 90 to 120 feet apart, with intermediate levels every 30 feet. Hoisting is done from only one level at a time through the same shaft. By this ingenious method every portion of blue ground is excavated and raised to the surface, the rubbish on the top gradually sinking and taking its place.

The scene below ground in the labyrinth of galleries is bewildering in its complexity, and very unlike the popular notion of a diamond mine. All below is dirt, mud, grime; half naked men, dark as mahogany, lithe as athletes, dripping with perspiration, are seen in every direction, hammering, picking, shovelling, wheeling the trucks to and fro, keeping up a weird chant which rises in force and rhythm when a greater task calls for excessive muscular strain. The whole scene is more suggestive of a coal mine than a diamond mine, and all this mighty organisation, this strenuous expenditure of energy, this costly machinery, this ceaseless toil of skilled and black labour, goes on day and night, just to win a few stones wherewith to deck my lady's finger! All to gratify the vanity of woman! "And," interposed a lady who heard this remark, "the depravity of man!"

With gems like diamonds, whose fabulous riches are concentrated into so small a bulk, it is not surprising that precautions against robbery are elaborate. The Illicit Diamond Buying (I.D.B.) laws are very stringent, and the searching, rendered easy by the "compounding" of the natives, is of the most drastic character. Formerly the favourite method of stealing diamonds was to swallow them, but when suspected, the personal inconveniences—in which certain powerful drugs took part—rendered this ingenious mode of stealing unpopular. It is, in fact, very difficult for a native employé to steal diamonds; were he to succeed, it would be almost impossible to dispose of them, as a potential buyer would prefer to secure the safe reward for detecting a theft rather than run the serious risk of doing convict work on the Cape Town Breakwater for a couple of years. I heard of a native who secreting a diamond worth several hundreds of pounds, after trying unsuccessfully to sell it, handed it back to the manager of his compound, glad to get the 6d. a carat to which he was entitled. Before the passing of the "Diamond Trade Act" the value of stolen diamonds reached nearly one million sterling per annum.

As a rule the better class of natives—the Zulus, Matabeles, Basutos, Bechuanas—when well treated, are honest and loyal. An amusing instance was told me of the devotion of a Zulu. He had been superintending a gang of natives on a small claim at the river washings near Klipdam. The claim yielded few stones, and the owner—my informant—sold the claim, handing over the plant and small staff, our friend the Zulu continuing to look after the business when

the new man took possession. In the course of a few months the purchaser became dissatisfied with his bargain, not a single diamond having turned up since the transfer. Soon after this the Zulu came to his old master in a mysterious manner, and laying a handful of diamonds on the table, said "There, Baas, are your diamonds; I was not going to let the new man have any of them!"

Depositing Floors.

Owing to the refractory character of blue ground fresh from the mines, it has to be exposed to atmospheric influences before it will pulverise under the action of water and mechanical treatment. It is brought to the surface and spread on the floors. Soon the heat of the sun and moisture produce a wonderful effect. Boulders, hard as ordinary sandstone when fresh from the mine, commence to crumble. At this stage the treatment of the diamonds assumes more the nature of farming than mining. To assist pulverisation by exposing the larger pieces to atmospheric influences, the ground is frequently harrowed and occasionally watered. The length of time necessary for crumbling the ground preparatory to washing depends on the season of the year and the amount of rain. The longer the ground remains exposed the better it is for washing. When the process is complete the softened friable blue clay is again loaded into trucks and taken to the washing machinery, where it is agitated with water and forced through a series of revolving cylinders perforated with holes about an inch in diameter; incorrigible lumps that will not pass the cylinders are again either subjected to the weathering process or passed between crushing rollers.

If a miner sees a diamond in a truck or in any of the blue ground in the mine, he has orders to secure it, and when he comes to the surface reports it to the manager of the compound. If a white labourer, he is then credited with 3s. a carat, and if a black 6d. a carat. For a diamond found on the depositing floors about half these sums are paid.

Washing and Concentrating Machinery.

The fine ground which has passed through the holes in the cylinder, together with a plentiful current of water, flows into the washing pans. These pans are of iron, 14 feet in diameter, furnished with ten arms, each having six or seven teeth. The teeth are set to form a spiral, so that when the arms revolve the teeth carry the heavy deposit to the outer rim of the pan, while the lighter material passes towards the centre and is carried from the pan by the flow of water. The heavy deposit contains the diamonds. It remains on the bottom of the pan and near its outer rim. This deposit is drawn off every twelve hours by means of a broad slot in the bottom of the pan. The average quantity of blue ground passed through each pan is from 400 to 450 loads in ten hours. The deposit left in each pan after putting through the above number of loads amounts to three or four loads, which go to the pulsator for further concentration.

The Pulsator.

The Pulsator is an ingeniously designed, somewhat complicated machine for dealing with the diamantiferous gravel already reduced one hundred times from the blue ground; the pulsator still further concentrating the gravel till the precious stones can be picked out by hand. The value of the diamonds in a load of original blue ground is about 30s., the gravel sent to the pulsator from the pans, reduced a hundred-fold, is worth £150 a load.

Mr. Fred Kirsten, an employé of the De Beer's Company,* made in 1897 the remarkable discovery that diamonds alone, of all minerals contained in the blue ground, adhere to grease, that all others will flow away as tailings over the end of the percussion table with the water. Now all the sorting (except for the very coarse size) is done by these machines,

* Specification of G. Labram, of Kimberley, for "A Method and Apparatus for Separating Diamonds from Earthy Matters." 24,260/97.

whose power of distinction is superior to the keenest eye of the native.

The diamond has a peculiar lustre, and on the sorter's table it is impossible to mistake it for any other stone. It looks somewhat like clear gum arabic, with a sort of intrinsic lustre which makes a conspicuous shine among the other stones.

Sometimes as many as 8000 carats of diamonds are separated in one day, representing about £10,000 in value.

About two million carats of diamonds are turned out of the Kimberley mines in a year, and by the end of 1904 ten tons of diamonds had come from these mines, valued at £60,000,000 sterling. This mass of blazing gems could be accommodated in a box five feet square and six feet high.

The diamond is a luxury for which there is only a limited demand. Ten years ago, from 4 to 4½ millions sterling were spent annually in diamonds. The last few years there has been no necessity to restrict the supply, and at the mines of the De Beers Company there is no keeping pace with the demand.

Prodigious diamonds are not so uncommon as is generally supposed. Diamonds weighing over an ounce (151·5 carats) are not unfrequent at Kimberley. Nine years ago, in one parcel of stones I saw eight perfect ounce crystals, and one inestimable stone weighing two ounces. The largest diamond from the Kimberley mines weighed 428½ carats, or nearly 4 ounces troy. It measured 1½ inch through the longest axis, and was 1½ inch square. After cutting, it weighed 228½ carats, losing 200 carats in the process. The largest known diamond has recently been discovered at the New Premier mine, about 20 miles W.N.W. of Pretoria. This mine is of the same type as the Kimberley mines, but much larger in size, and in fact it is the largest known diamantiferous pipe in the world,—the pipe containing the "blue ground" along the longer diameter of its oval-shaped cross-section measuring over half a mile, the area of which is estimated at 350,000 square yards. This pipe breaks through felsitic rocks. The diamond, called "Cullinan" from the name of one of the directors of the Company on whose farm it was discovered, weighs no less than 3025½ carats, or 9586·5 grains (1·37 lbs. avoirdupois). It is a fragment, probably less than half, of a distorted octahedral crystal; the other portions still await discovery by some fortunate miner. Through this unequalled stone I passed a beam of polarised light in various directions, and could see colours in all cases, the brightest appearing when the light passed along the greatest diameter—about four inches. Here the colours were very fine, but no regular figure was to be seen. These observations show that the diamond is in a state of internal strain.

The clearness throughout is remarkable, the stone being absolutely limpid like water, with the exception of a few flaws, dark graphitic spots, and coloured patches close to the outside. At one part near the surface there is an internal crack, showing well the colours of thin plates. At another point there is a milky, opaque mass, of a brown colour, with pieces of what may be iron oxide. There are four cleavage planes of great smoothness and regularity. On other parts of the surface the crystalline structure is very marked. The edges are rounded in parts, and triangular markings (depressions) are to be seen. I also noticed square depressions, nearly as sharp and perfect as the triangular ones. Gigantic as is the Cullinan diamond, it represents in weight less than half the daily output of the De Beers mines, which averages about 7000 carats per day.

Next in size to the "Cullinan" comes the one which was found at the Jagersfontein mine. It weighed 970 carats—over half a pound.

I will show you on the screen the relative sizes of some large or famous diamonds.

1. Koh-i-noor, after the second cutting, 106 carats.
2. Loterie d'Angleterre, 49 carats.
3. Nizam of Hyderabad, 279 carats.
4. Orloff, 194 carats.
5. Koh-i-noor, after first cutting, 279 carats.
6. Regent or Pitt, 137 carats.

7. Duke of Tuscany, 133 carats.
8. Star of the South, 124 carats.
9. Pole Star, 40 carats.
10. Tiffany, yellow, 125 carats.
11. Hope, blue diamond, 44 carats.
12. Sancy, 53 carats.
13. Empress Eugenie, 51 carats.
14. Shah, 86 carats.
15. Nassak, 79 carats.
16. Pacha of Egypt, 40 carats.
17. The Cullinan, 3025 carats.
18. Excelsior, Jagersfontein, 969 carats.

The Diamond Office.

From the sorting room the stones are taken to the Diamond Office to be cleaned in acids and sorted into classes by the valuers, according to colour and purity. It is a sight for Aladdin to behold the valuers at work in the strong-room of the De Beers Company. In the Kimberley treasure store the tables are literally heaped with stones won from the rough blue ground—stones of all sizes, purified, flashing, and of inestimable price; stones coveted by men and women all the world over; and last but not least stones that are destined to largely influence the development and history of a whole huge continent.

The Compound System

One great safeguard against robbery is the "compound" system of looking after the natives. A "compound" is a large square, about 20 acres, surrounded by rows of one-storey buildings of corrugated iron. These buildings are divided into rooms each holding about twenty natives. Within the enclosure is a Store where the necessaries of life are supplied at a reduced price, and wood and water free of charge. In the middle is a large swimming-bath with fresh water running through it. The rest of the space is devoted to games, dances, concerts, and any other amusement the native mind can desire. In case of accident or illness there is a well-appointed hospital where the sick are tended. Medical supervision, nurses, and food are supplied free by the Company.

In the compound are to be seen representatives of nearly all the picked types of African tribes. Each tribe keeps to itself, and to go round the buildings skirting the compound is an admirable object-lesson in ethnology. At one point is a group of Zulus; next we come to Fingoes; then Basutos; beyond come Matebele, Bechuanas, Pondos, Shangains, Swazis, and other less known tribes, either grouped or wandering around making friendly calls.

The clothing in the compound is diverse and original. Some of the men are evident dandies, whilst others think that in so hot a climate a bright coloured handkerchief or "a pair of spectacles and a smile" is as great a compliance with the requirements of civilisation as can be expected.

The natives are not interfered with in their various amusements, always provided they do not make themselves objectionable to their neighbours. They soon learn that tribal animosities are to be left outside the compound. One Sunday afternoon my wife and I walked unattended about the compound, almost the only whites present among 1700 natives. The manners of the fold were so friendly, and their smiles so cordial, that the idea of fear vanished. At one part a Kaffir was making a pair of trousers with a bright nickel-plated sewing-machine, in which he had invested his savings; next to him a "boy" was reading from the Testament in his own language to an attentive audience; in a corner a party were engaged in cooking a savoury mess in an iron pot; further on the orchestra was tuning up, and Zulus were putting the finishing touches to their toilet of feathers and beads. One group was intently watching a mysterious game. It is played by two sides, with stones, and grooves and hollows in the ground, and appears of most absorbing interest. It seems to be universal throughout Africa; it is met with among the ruins of Zimbabwe, and signs of it are recorded on old

Egyptian monuments. I wanted to learn it, and an intelligent Zulu player offered to teach it to me in a few minutes. Captain Dallas, however, with a more accurate opinion of my sharpness than my friend the Zulu, assured me it would take months of study before I could begin to know anything about it. He had tried for years, and could make nothing of it.

They get good wages, varying according to occupation. The work is appreciated, and there are always more applicants than can be accepted. On entering, the restrictions to which they must submit are fully explained, and they are required to sign for three months at least, during which time they must not leave the compound or mine. It is seldom that a man does not return, once he has lived the life in the compound; some come again and again for years, only leaving occasionally to spend accumulated savings. The most careful men save money, and carry it at intervals to the superintendent to keep for them. Occasionally they ask to look at their savings, which may amount to £30 or £40, accumulated by dribblets. They are ignorant of savings banks or interest, and are content if they see their own money in the original rags and papers in which it was handed in. The Kaffir, on demand, must behold his coins just as he handed them in, wrappings and all. Sometimes the superintendent will have as much as £1000 of savings in his care.

(To be continued).

THE DETECTION OF METHYL ALCOHOL.*

By HEYWARD SCUDDER.

THE tests for the detection of methyl alcohol are used chiefly to distinguish it from ethyl alcohol, so their value is dependent first on a sharp distinction from ethyl alcohol, then on their delicacy and rapidity. In the following description the standard of delicacy will be taken as the quantity of methyl alcohol that can be detected in ethyl alcohol. Most of the tests will show very much smaller quantities of methyl alcohol in water, but their use for such a purpose is practically unknown.

Odour Tests.

This is made by adding to the solution salicylic acid and concentrated sulphuric acid and warming, thus forming methyl salicylate, which is supposed to have a characteristic odour (of oil of wintergreen). In experiments made on eight persons I found that none of them could distinguish between ethyl and methyl alcohol by this test, because the odour of ethyl salicylate so strongly resembles that of methyl salicylate. If told that both alcohols were present a difference in odour was often noticed, but if solutions of unknown content were given, e.g., two tubes of methyl or two of ethyl alcohol, the test failed even when comparative tests with the alcohols were made.

All tests dependent on odour are unsatisfactory, because it is impossible to make accurate comparative tests. After smelling any odiferous body, probably on account of persistence of the odour in the nasal passages, or possibly from slow reactivity of the olfactory nerves, it is not possible for an ordinary person to have an accurate perception of the odour of a second body. This can readily be shown experimentally, most surprising mistakes being made after the sense of smell is once blunted. In making colour tests the comparison is direct and the subjective effect of memory is eliminated.

I have been told that this test has been used in trials, for adulteration of liquors, to show juries the difference between the two alcohols, the point being made that there is a difference in the rapidity of the production of the odour as well as in the quality. I consider the test unre-

liable and not sufficiently rapid to be an improvement on the test by oxidation with a hot copper spiral and testing for the oxidation product by resorcin. The difference in colour between the condensation products of acetaldehyde and resorcin and formaldehyde and resorcin is great enough to be appreciated by any juror.

(Sieker, *Pharm. Review*, 1901, xix., 19, 117, and Chomezki, *Farmaz. Vestnik*, lxxxix., 167—abstract *Fres. Zeit.*, 1905, xlv., 44, 124, give tests for methyl alcohol depending on the recognition of the odour of formaldehyde after oxidation. They recommend the test for use in the case of drugs, &c., where many compounds are present. The tests are not very delicate).

Colour Tests.

In the Riche and Bardy (*Comptes Rendus*, 1875, lxxx., 1076), test the methyl alcohol is converted into methyl aniline, which is then tested for. The test is too long and slow to be of much use to-day.

In all the other tests the alcohol is oxidised to formaldehyde, methylal, or formic acid. The colour test is then applied to this oxidation product. Methylal gives the same reaction as formaldehyde in almost all tests. If ethyl alcohol is present, either the colour test must be given only by the oxidation product of methyl alcohol as in oxidation to the acid, formic acid giving a dark colour with silver nitrate, while acetic acid gives no colour—or enough of the corresponding oxidation product of ethyl alcohol must be removed to prevent interference with the colour. The difficulty of fulfilling these conditions is the chief cause of failure in the tests used. It is practically impossible to control oxidation so as to get a good yield of formic acid, and the tests for its detection are not very delicate. The removal of all the acetaldehyde without some loss of formaldehyde is impossible, but this method is perfectly practicable since the tests for formaldehyde are extremely delicate. The fact that pure ethyl alcohol when oxidised by any of the methods used in the tests for methyl alcohol gives some formaldehyde, is not sufficiently considered. It has been shown (Mulliken, Scudder, *Am. Chem. Journ.*, 1900, xxiv., 446) that when ethyl alcohol is oxidised by a heated copper spiral, formaldehyde is formed in small amounts. I have found that this is also true when ethyl alcohol is oxidised in cold dilute solution by potassium bichromate and sulphuric acid, or by potassium permanganate and sulphuric acid, enough formaldehyde being made to give the gallic acid test.

Therefore, it is obvious that the test used to show the presence of formaldehyde, after oxidation of the alcohol, must not be too delicate, or it will apparently show the presence of methyl alcohol when none is really there. This is the defect of the gallic acid reaction,* an extremely characteristic test for formaldehyde and one little obscured by the presence of other compounds, but so delicate that it is given by solutions of ethyl alcohol, cane-sugar, and a great variety of compounds after oxidation by a heated copper spiral (Mulliken, Brown, and French, *Am. Chem. Journ.*, 1904, xxv., 115).

The tests that follow are grouped by the reagent used for the production of the colour, in order to make more clear a general understanding of the difficulties and of the sources of error.

Reagent, Silver Nitrate.

Miller Test (Allen's "Commercial Organic Analysis," 3rd Ed., vol. i., p. 81).—This consists in oxidation in the cold by potassium bichromate and sulphuric acid, distillation, and testing the distillate for formic acid by silver nitrate. Allyl alcohol and acetone are said to give the same reaction. It is noted that a trace of formic acid or some other reducing agent is formed from ethyl alcohol. The test is not delicate and is of little importance.

* The solution to be tested is mixed with 0.2 c.c. of a saturated alcoholic solution of gallic acid and poured on top of (not mixed with) concentrated sulphuric acid in a test-tube. A contact ring of blue or green and blue shows the presence of formaldehyde.

* Presented before the New York Section of the American Chemical Society. From the *Journal of the American Chemical Society*, July, 1905.

Reagent, Lead Peroxide.

Trillat test (*Ann. Chim. Anal. Appl.*, 1899, iv., 42; *Comptes Rendus*, 1899, cxviii., 138; *Bull. Soc. Chim.*, [3], 1899, xxi., 445).—This consists in oxidation in cold dilute solution by potassium bichromate and sulphuric acid, under which conditions methyl alcohol is said to give methylal, ethyl alcohol to give acetaldehyde, acetal, and acetic acid. The acetaldehyde is removed by distilling 25 c.c. The next 100 c.c. distilled contain the methylal. One-half of this is digested in a closed flask with dimethylaniline at 70–80° for three hours, forming tetramethyldiaminodiphenylmethane. The solution is made alkaline and the excess of the dimethylaniline distilled off. The residue is acidified by acetic acid and a little lead peroxide added. On boiling, a blue colour appears if methyl alcohol is present. It is said to show 0.2 per cent methyl alcohol in ethyl. The time required for the test is about five hours.

The difficulties are numerous. If all the acetaldehyde is not removed by the fractional distillation, what remains may give a colour that resembles or interferes with that from methylal. Since some methylal distils over with the acetaldehyde it is not safe to distil off much more than 25 c.c. to remove the latter, for if only a small amount of methyl alcohol is present, the loss might be sufficient to spoil the test. The dimethylaniline and the lead peroxide must be very pure or the colour may be affected. In distilling off the excess of dimethylaniline (this procedure is necessary because dimethylaniline gives a violet or blue colour with lead peroxide) some methylal is lost, as may be shown by tests. I have found it easy to be sure of the removal of all the dimethylaniline, by filtering through a wet filter before distilling. No special care is necessary in acidifying after the removal of the dimethylaniline, since a great excess of acetic acid has no effect on the colour. The amount of lead peroxide used is actually a variable quantity. The directions call for four to five drops of a suspension in water. In addition to the variable strength of different samples, another error is possible here, since the amount of lead peroxide present will depend on how thoroughly the suspension is shaken before use. If too little is used, the colour is faint. If too much is used, the colour changes from blue to brown, though the effect of heat in deepening the colour still persists.

The depth of colour is supposed to be proportional to the amount of methyl alcohol originally present, but it is sometimes difficult to get this result. I have found a much fainter colour from a solution that contained 10 per cent methyl alcohol than from one that contained 1 per cent, though the procedure was the same in each case.

I believe that the development or deepening of the colour by boiling is characteristic. Acetaldehyde, after digestion with dimethylaniline and subsequent treatment as in the Trillat test, gives in the cold a colour varying from green-yellow to green-blue. Dimethylaniline in the cold gives with lead peroxide a colour varying from green-yellow to pure blue. But in both cases the colour does not deepen on boiling, while the blue from methyl alcohol develops only on boiling. The colour may be diminished or changed by the use of the wrong amount of lead peroxide, but here again boiling makes a characteristic deepening, if methyl alcohol was in the original solution tested, so that if there is a colour in the cold that disappears or is not deepened by boiling, no methyl alcohol is present (provided the test has gone well). If the colour deepens on boiling, even if it is not a pure blue but possibly a green-blue or brown, methyl alcohol is present.

Wolf (*Ann. Chim. Anal. Appl.*, 1899, iv., 183) states that pure ethyl alcohol gives the same reaction as methyl when the Trillat test is used, but that if the digestion with dimethylaniline is made at room temperature for twenty-four hours instead of at 70–80° for three hours the test works perfectly. He claims that 0.1 per cent of methyl alcohol can be shown in ethyl alcohol in this way. Since he makes no statement of the effect of heat on the colour, the value of the improvement is doubtful, for it is possible

that the colour obtained from ethyl alcohol was due to the incomplete removal of acetaldehyde.

Robine* gives an elaborate criticism of the Trillat test, and suggests several small changes in the procedure. His most essential points are the recommendation to make a blank test of every fresh sample of dimethylaniline; the necessity for having pure lead peroxide and for using the proper amount; the difficulty of removing all the acetaldehyde without loss of methylal; and the fact that the test is spoiled unless all the acetaldehyde is removed. The presence of acetaldehyde is sometimes indicated by a yellow colour of the solution and a precipitate of aldehyde resin after the excess of dimethylaniline has been distilled off. His criterion for the presence of methyl alcohol is that the final test must give a pure blue appearing hot, disappearing cold. Any shade of blue that has green in it, green-yellow, or pure green, is not to be regarded, since it may come from incomplete removal of acetaldehyde.

Since Robine notes the effect of heat on the colour, it would appear probable that he tried heating in the cases where the colour was due to acetaldehyde, but the fact that in such cases no deepening occurs when the solution is boiled is not mentioned by him. This differs from my observations previously given.

It is evident that the Trillat test must be used with care. It is delicate and fairly rapid, but the test may be spoiled not only by slight variations in the procedure, but also by causes of unknown origin which occur when the procedure is strictly followed. It is certainly not a test to be recommended to persons of limited knowledge of chemistry.

(To be continued).

THE FORMATION OF OZONE BY ULTRA-VIOLET LIGHT.

By FRANZ FISCHER and FRITZ BRAEHMER.

LENARD (*Ann. Phys.*, 1900, i., 486) first observed that ultra-violet light is capable of ozonising oxygen. When he allowed the light of a spark-gap to act upon oxygen through a quartz plate (transparent to ultra-violet) ozone was formed. But no ozone was formed if the light had also to penetrate a sheet of mica (opaque to ultra-violet).

Goldstein (*Berichte*, 1903, xxvii., 3042) noticed a small amount of ozone outside Geissler tubes as soon as a discharge was sent through them, but only if they were partly made of quartz. He regarded this as an effect of ultra-violet light, and it is very probable that the ozone, which he condensed by means of liquid air in the interior of his tubes, thus in the region of electric discharge, owes its formation to ultra-violet radiation.

Warburg (*Ann. Phys.*, 1904, xiii., 475) has shown that during the so-called silent electric discharge, e.g., in Siemens' ozone tubes, ultra-violet light and cathode rays appear, and it seems to him that the cause of the formation of ozone is to be found in the appearance of these rays.

Warburg and Regener (*Sitzungsber. Preuss. Akad. d. Wiss.*, 1904, 1228) allowed the ultra-violet light of a spark-gap to act upon pure oxygen in the quartz capillary of their differential ozonometer, and measured the contraction of volume. They also allowed the rays to act upon strongly ozonised oxygen, and determined its increase of volume. From their measurements they conclude that besides an ozonising radiation, disozonising rays are also at work, and their curves for ozonisation and disozonisation intersect at 2.2 per cent ozonisation; i.e., under Warburg and Regener's conditions at 2.2 per cent ozonisation the rates of formation and decomposition are equal.

For our purpose, i.e., the determination of the conditions of formation and the relative yields on ozonising oxygen

* *Ann. Chim. Anal. Appl.*, 1901, vi., 128, 171; cf. Huler (*Ber.*, 1904, xxxvii., 3417) and Bach (*ibid.*, 1904, xxxvii., 3986) on the unreliability of the Trillat test for formaldehyde, which is the same as the methyl alcohol test beginning with the digestion with dimethylaniline.

by ultra-violet light, the quartz mercury arc lamp, which is rich in ultra-violet rays, seemed to us specially suitable (A. Pfüger, "Die Quecksilberlampe als Ultra-violette Lichtquelle," *Phys. Zeit.*, 1904, v., 414; Ladenburg, "Spectrale Energieverteilung der Quecksilberlampe aus Quarzglas," *Phys. Zeit.*, 1904, v., 525); it is already known that its radiation ozonises the air. We used for this purpose a lamp of the form previously described by one of us (*Berichte*, 1905, xxxviii., 2630).

Pure oxygen was used for the investigation. This was prepared electrolytically from dilute sulphuric acid, was led through glass-wool and then over heated platinised asbestos, so that any admixed ozone in it was destroyed and traces of hydrogen were oxidised to water. Then the oxygen passed into a so-called intensive washing flask with concentrated sulphuric acid, and then entered the quartz vessel of the mercury lamp between the second quartz wall and the glass condenser cooled with water. The oxygen containing ozone left the lamp through the middle of the glass condenser.

In an absorption apparatus, closed by means of mercury, iodine was separated out from neutral potassium iodide solution by means of the ozone. In all experiments the procedure adopted was the same. In the absorption tube 20 c.c. of $N/10$ potassium iodide solution were placed; it was always washed out with the same volume of water, acidulated with 20 c.c. of $N/10$ sulphuric acid solution, the same volume of starch solution of constant concentration added, and the iodine separated was finally titrated with $N/100$ sodium thiosulphate solution.

The lighting of the lamp was effected by means of a small inductor. The discharge space of the lamp was permanently connected with a mercury air-pump, and the vacuum was regulated partly by means of this and partly by means of an absorption tube which contained ignited carbon, and was placed in liquid air.

The following are the chief points which were considered in this research:—

1. Effect of cooling the gas.
2. Influence of strength of the light of the lamp.
3. Influence of the velocity of the current of gas.
4. Influence of the degree of purity of the gas.

1. Effect of Cooling the Gas.

In consequence of the rapidly increasing rate of destruction of the ozone with rising temperature (Clement, "Bildung des Ozons bei Hoher Temperatur," *Ann. Phys.*, 1904, xiv., 334) it was to be expected that the cooling of the gas exposed to the rays of the lamp would have a considerable effect upon the obtainable concentration of the ozone.

If we led the gas without any cooling through the lamp, at the same time allowing no water to flow through the glass condenser, no appreciable amount of ozone was obtained.

The measurement of the temperature, which was quickly produced as soon as the vessel was closed, although the quartz vessel had double walls and the space between the two walls was carefully exhausted, afforded an explanation. We found a minimum temperature of 27° , at which temperature it has long been known that ozone cannot exist. But if water was sent through the condenser, the gas, passing through the narrow space (1 m.m. wide) between the inner warmed quartz wall and the outer wall of the glass condenser which was kept cold, cooled the quartz wall, and very considerable quantities of ozone were found.

(a). *Effect of the Velocity of the Water.*—In Table I. the cooling water at 15° possessed only two-thirds of the velocity in Table II. The tables give under "No." the number of the experiment, under "A.L." and "A.E." the current strength in the lamp and the electrolyser producing oxygen respectively; under "titration" are given the c.c. of $N/100$ thiosulphate which were needed to titrate the iodine separated by the ozone, under "Mg. O_3 " the amount of ozone calculated from this, and under "weight per cent

O_3 " the percentage of ozone present in the oxygen. For this the total weight of the oxygen was calculated from the current strength in the electrolysing apparatus. The experiments always lasted fifteen minutes.

TABLE I.

No.	A.L.	A.E.	Titration.	Mg. O_3 .	Weight per cent O_3 .
1.	5.1	3.01	1.69	0.406	0.182
2.	5.1	3.01	1.80	0.432	0.193
3.	5.1	3.01	1.81	0.434	0.194

TABLE II.

No.	A.L.	A.E.	Titration.	Mg. O_3 .	Weight per cent O_3 .
1.	5.1	3.01	2.03	0.487	0.217
2.	5.1	3.01	2.05	0.492	0.219
3.	5.1	3.01	2.06	0.494	0.221

Comparison of Tables I. and II. shows that with increasing velocity of the cooling water, *i.e.*, increased cooling, the amount of ozone formed increases, so that if the strength of the gas current remains the same the percentage becomes greater.

(b). *Effect of the Temperature of the Water.*—In order to determine the influence of the temperature directly, the water was forced at a constant weight through the glass condenser by means of a pump driven by an electro-motor. The circulation of the water was as follows:—From the pump it passed through an externally cooled lead pipe through a vessel with thermometer 1, through the glass condenser, through a vessel with thermometer 2, and back to the pump. T_1 and T_2 give the temperatures of the water before entering and after leaving the glass condenser respectively. The velocity of the water was considerably less than that of the condenser water.

TABLE III.—Lead Tubing Cooled Externally by Water at the Temperature of the Room.

No.	A.L.	A.E.	T_1 .	T_2 .	Titration.	Mg. O_3 .	Weight per cent O_3 .
1.	5	3	21.5°	22.5°	1.35	0.324	0.145
2.	5	3	22	23	1.61	0.386	0.173
3.	5	3	22	23	1.62	0.389	0.174

TABLE IV.—Lead Tubing Cooled Externally with Ice.

No.	A.L.	A.E.	T_1 .	T_2 .	Titration.	Mg. O_3 .	Weight per cent O_3 .
1.	5	3	$+1^{\circ}$	$+2^{\circ}$	1.81	0.434	0.194
2.	5	3	$+1$	$+2$	1.79	0.430	0.192
3.	5	3	$+1$	$+2$	1.81	0.434	0.194

TABLE V.—Calcium Chloride Solution used in the Circuit instead of Water. Lead Tubing Cooled Externally by means of a Cooling Mixture.

No.	A.L.	A.E.	T_1 .	T_2 .	Titration.	Mg. O_3 .	Weight per cent O_3 .
1.	5	3	-10°	-2.5°	2.27	0.545	0.244
2.	5	3	-10	-2.5	2.4	0.576	0.258
3.	5	3	-10	-2.5	2.21	0.530	0.237

Comparison of Tables III., IV., and V. shows clearly the influence of the temperature of the cooling liquid. As the temperature falls the percentage of gas rises considerably.

As the lamp burns under water, it does not appear possible that the increased cooling in the glass condenser has any appreciable cooling effect upon the lamp, and thus influences the nature of the light emission in a manner favourable to the formation of ozone.

2. Influence of the Strength of the Light.

The cooling was kept constant, and also the current of the gas (as far as possible), and the current through the lamp—and hence the strength of the light—was varied. The potential of the lamp amounted to, roughly, 20 volts.

Thus at first the yield of ozone increases with increasing strength of light, but finally decreases. In our opinion, the decrease is due to the fact that finally, as the current through the lamp goes on increasing, the temperature is raised too high, and then the rate of decomposition of the ozone formed assumes appreciable values.

TABLE VI.

No.	A.L.	A.E.	Titration.	Mg.O ₃ .	Weight per cent O ₃ .
1.	2	2'96	1'68	0'403	0'183
2.	2	2'99	1'68	0'403	0'181
3.	3	3'01	2'00	0'480	0'214
4.	3	3'00	2'00	0'480	0'215
5.	6'5	3'00	2'09	0'502	0'224
6.	6'5	3'00	2'10	0'504	0'226
7.	8	3'00	2'02	0'485	0'217
8.	8	3'00	2'04	0'490	0'219

3. Influence of the Strength of the Gas Current.

The cooling effect of the gas upon the quartz wall we have already mentioned. It was therefore to be expected that, on increasing the velocity of the gas current, the absolute quantity of ozone produced would be increased—firstly, because the cooling effect upon the quartz wall would be increased; and, secondly, because the ozone, being more quickly removed, would be protected from warming and thus from decomposition. The percentage of ozone in the gas, however, would probably be decreased. Table VII. confirms our suppositions.

TABLE VII.

No.	A.L.	A.E.	Titration.	Mg.O ₃ .	Weight per cent O ₃ .
1.	5	2'03	1'59	0'382	0'253
2.	5	2'06	1'59	0'382	0'249
3.	5	3'09	2'20	0'528	0'230
4.	5	3'10	2'25	0'540	0'234
5.	5	3'95	2'47	0'593	0'201
6.	5	4'00	2'38	0'571	0'192

Thus we see that, on doubling the strength of the gas current (from 2 to 4 ampères), the absolute amount of ozone produced by the lamp is also nearly doubled, while, on the other hand, the percentage amounts to only four-fifths of the first percentage. Whether on further increasing the strength of the gas current the yield is also proportionately increased is not yet known.

4. Influence of the Purity of the Oxygen.

We have finally allowed our pure oxygen to contain different amounts of water-vapour, drying it once only with calcium chloride and the other time with concentrated sulphuric acid. For the present, however, we cannot report any definite results.

On the basis of the preceding results we may summarise as follows:—

The ozonisation of oxygen by means of ultra-violet light results if the temperature of the gas is not too high. Practically it does not occur at all if the gas has a temperature above 270°, because then the reaction $3\text{O}_2 \rightleftharpoons 2\text{O}_3$, in consequence of the supply of heat, proceeds from right to left more rapidly than it goes from left to right, in consequence of the absorption of the energy of ultra-violet light. These results agree with those of Clement (*loc. cit.*) from the Nernst Institute, according to which the rate of decay of ozone rapidly increases with increasing temperature. They also explain the fact that, with Heraeus' quartz mercury lamp, for example, the smell of ozone decidedly decreases soon after the lamp has been lighted. The ozone forming on that lamp's simple quartz wall, which becomes hot, again decomposes in consequence of the heat, so that very little ozone is formed near the hot quartz. The gradually occurring alteration in the spectral distribution of the light might indeed act in the same way.

The effects of the strength of the light of the lamp, which have been repeatedly confirmed, and also of the cooling and velocity of the gas current, agree perfectly with what is known concerning the influence of the silent electric discharge on ozone formation, for example, in Siemens' ozone apparatus, and seem to be a proof of the correctness of Warburg's view (*loc. cit.*) that the formation of ozone by the silent electric discharge is due to the ultra-violet light thus formed.

A short time ago one of us showed that the lamp used by us can produce in a few hours the violet colouration of glasses containing manganese, which is effected by sunlight in high mountainous regions in months and years, and in our low regions only after longer periods, because the ultra-violet part of its spectrum is strongly absorbed by the earth's atmosphere.

By this absorption of ultra-violet sunlight by our atmosphere, as is universally accepted on the basis of Lenard's observations (*loc. cit.*), ozone results in the upper layers of air; when it sinks to lower regions it is decomposed by oxidisable substances.

We are at present engaged in altering our apparatus in order to free ourselves more from the disturbing effects of the radiation of heat. As we require some time for this purpose, we publish here the results we have obtained up to the present. As far as we can see from preliminary experiments, the yield of ozone is capable of being considerably increased.—*Berichte*, 1905, xxxviii., 2633.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 7, August 14, 1905.

The Gases Evolved from Actinium.—A. Debierne.—The author performs a large number of experiments with a solution of radium bromide and with salts of actinium, both in solution and in the solid state, and finds that helium is evolved on heating both sets of salts. The gaseous mixture evolved is introduced into a glass tube containing different substances for absorbing all the gases which react chemically. Thus the oxygen, hydrogen, gaseous carbides, and nitrogen, besides other compound gases, are got rid of, leaving only the gases of the argon group. These are transferred into a small capillary tube with two electrodes and the spectrum photographed and examined. It is evident from the control experiments performed by the author that the helium results from the presence of the radio-active bodies.

The Dense Liquids containing Alkaline Iodo-mercurate Bases.—M. Duboin.—The author investigates the heavy liquid consisting of a saturated solution of mercury iodide in a solution of potassium iodide. He then attempts to prepare still heavier liquids by replacing the potassium iodide by other alkaline iodides—those of sodium, lithium, and ammonium. The density of potassium iodo-mercurate is 3'196 at 22'9°; of sodium iodo-mercurate solution, 3'46 at 26°; of lithium iodo-mercurate solution, 3'28 at 25'6°; and of ammonium iodo-mercurate, 2'98 at 26°. The liquid containing the sodium salt gives with excess of water a dense precipitate of mercuric iodide, which dissolves without decomposition in alcohol. Owing to this fact, the sodium iodo-mercurate solution is very useful for the separation of minerals and determination of their densities. This compound also dissolves without decomposition in a large number of organic liquids, such as methylic and ethylic alcohols, ethylic and benzylic aldehydes, acetone, formic, acetic, propionic, butyric, and valeric acids, besides ethyl acetate and oxalate.

Nos. 8 and 9, August 21 and 28, 1905.

These two numbers contain no chemical matter.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxviii., No. 11, 1905.

Hydrolysis of Tin Chloride and Bromide.—P. Pfeiffer.—If tin tetrachloride is dissolved in water, ether added, and the ethereal layer evaporated, a white crystalline mass is obtained. Analysis shows that these crystals have the composition represented by the formula

$\text{SnCl}_3\text{OH} + \text{H}_2\text{O} + (\text{C}_2\text{H}_5)_2\text{O}$. The corresponding bromide compound can be prepared similarly. These compounds are undoubtedly the intermediate products of the hydrolysis of the tetrachloride and tetrabromide respectively. The "alcoholysis" of the tin haloids proceeds similarly in its first stages, $\text{SnCl}_3\text{OC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH}$ being formed. Since tin tetrachloride is not an electrolyte, and alcohol possesses only a very small power of dissociating dissolved substances, the process in both hydrolysis and alcoholysis is purely chemical, and is to be explained without the aid of ionic reactions. In the author's opinion, when tin tetrachloride (or tetrabromide) reacts with water, hydrates are first formed, which then in presence of excess of water give up hydrochloric (or hydrobromic) acid, and yield the intermediate product, $\text{Sn}^{\text{Cl}_3}_{(\text{OH})_x} \rightarrow \text{Sn}^{\text{Cl}_3}_{(\text{OH})_{x-1}}$. By the repetition of this process stannic acid is finally produced.

Ultramarine Blue.—K. A. Hofmann and W. Metzener. —Although ultramarine, unlike other blue dyes, is rapidly decomposed by dilute acids or solutions of salts with acid reactions, it is perfectly stable in presence of concentrated sulphuric acid or glacial acetic acid. Thus ultramarine S may be kept in a closed flask with 98.5 per cent sulphuric acid for six weeks at ordinary temperatures without suffering the least change of colour; with 93 per cent acid a change begins to occur after twelve hours, and with 89 per cent acid after three hours. Fuming sulphuric acid does not affect ultramarine blue at ordinary temperatures, and, moreover, protects it against the action of fuming nitric or nitrous acid, which would otherwise oxidise the sulphur group. On investigating quantitatively the behaviour of ultramarine with acetic acid and 20 per cent acetic anhydride, it was found that neither the "colour part" nor the "silicate part" is affected. This behaviour is very different from that of thiosulphate and polysulphide, and seems to the author to be analogous to the behaviour of compounds of sulphur with anhydrides, of which as yet only Weber's blue sesquioxide S_2O_3 is known.

New Reagent for Nickel.—L. Tschugaeff. —The most sensitive test for nickel is the brown colouration produced by alkali thiocarbonates, but this reaction is considerably affected by the presence of cobalt. The author has found that α -dimethylglyoxime, $\text{CH}_3\text{C}(\text{N.OH})\text{C}(\text{N.OH})\text{CH}_3$, is an exceedingly sensitive and characteristic reagent for nickel. The solution to be tested is freed from excess of acid by the addition of alkali (preferably ammonia or sodium acetate solution), the powdered dioxime is added, and the solution boiled for a short time. A scarlet precipitate of the composition $\text{NiD}.\text{DH}_2$ (DH_2 =dioxime) is produced. If the nickel is present only in very small quantity a yellowish solution is first obtained, from which the red compound separates out on cooling. By this test it is quite easy to demonstrate the presence of nickel in solutions containing only 1 part of nickel in 400,000 parts of water. The reaction is not in the least influenced by the presence of about ten times the quantity of cobalt. But as the cobalt salts form brown compounds with α -dimethyl glyoxime, if larger quantities of cobalt are present it is better to proceed as follows:—A large excess of ammonia is added to the solution to be tested, which is then thoroughly shaken up. Any cobalt salts present are thus converted into the cobalt ammonia compounds. Excess of dioxime is then added, and the solution boiled for a short time. When larger quantities of nickel are present (e.g., in commercial cobalt salts) a scarlet scum forms on the walls of the test-tube, but it is generally necessary to cool, filter, and wash the residue with water. If nickel is present it appears pink, colourless if nickel is absent. In this way 0.1 m.grm. of nickel can be detected in 500 m.grms. of cobalt. Dimethyl glyoxime can now be obtained commercially.

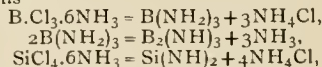
Oxidation of the Nitrogen of the Air by means of the Electric Arc.—F. v. Lepel. The author uses electrodes which rotate in opposite directions, the anode

consisting of oxidised copper-wire and the cathode of pyrolusite. The colour of the flame is pale greenish yellow or greenish white. The furnace must be wide and roomy, for narrow tubes give smaller yields, and, moreover, favour cooling. A very large absorption chamber, into which water vapour and warm water are introduced, is necessary, and the air must be passed into the furnace obliquely at the rate of about 180 litres an hour. Carbon cathodes are found to be superior to those of pyrolusite. Increasing the length of the flame increases the yield.

Formaldehyde and the Production of Formates.—Hans and Astrid Euler.—Formaldehyde is a feeble acid forming salts with strong bases. A normal solution of formaldehyde mono-sodium salt contains about half the salt as such, while half is split up into free base and free formaldehyde. In dilute solution the formaldehyde salts behave like binary electrolytes; the dissociation constant of the aldehyde as acid amounts to roughly $1 \cdot 10^{-14}$ at 0° . The formation of sodium or barium formate from formaldehyde and sodium or barium hydroxide is a reaction of the second order. If the formaldehyde is present in great excess (thus if its concentration is practically constant), the reaction is of the first order. The value of the constant decreases slightly with the time. The behaviour of caustic soda is very similar to that of barium hydroxide, and the reaction constants are nearly the same, decreasing somewhat as the initial concentration of the formaldehyde rises, on account of the formation of formaldehyde salts. The production of formate is simply a decomposition process, and not an oxidation, for the reaction occurs as quickly in an atmosphere of hydrogen as in an atmosphere of oxygen. Formate is produced much more quickly with lime than with sodium or barium hydroxide. Even if no sugar is formed the dissolved bases possess a specific power of producing formate, and the power of different bases of condensing formaldehyde to sugar is not directly connected with the rate of producing formate.

Effect of Silver Nitrate upon the Solubility of Silver Nitrite.—R. Abegg and H. Pick.—The authors find that the solubility relations of silver nitrite are simply and accurately expressed by Nernst's theory, and they explain the fact that Naumann and Rücker have recently obtained different results by supposing that their mistake is due to their assumption that silver nitrate, being a very difficultly soluble salt, may be regarded as being completely split up into its ions. This by no means always holds good for difficultly soluble salts. While neutral salts are often completely dissociated at a concentration of 0.1 molecule per litre, there are also salts which, at the saturation concentration of only 0.0001, form practically no ions, e.g., HgI_2 .

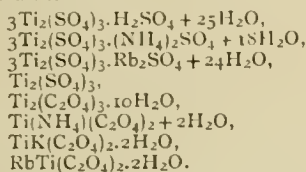
Zirconium Halogen Compounds.—Arthur Stähler and Bruno Denk.—The authors have prepared addition products of zirconium chloride, iodide, and bromide with ammonia, viz., $\text{ZrCl}_4.8\text{NH}_3$, $\text{ZrI}_4.8\text{NH}_3$, $\text{ZrBr}_4.10\text{NH}_3$. The formation of these addition products may be regarded as analogous to the process of taking up water of crystallisation by the so-called complex salts. The similar compounds of boron and silicon, i.e., $\text{BCl}_3.6\text{NH}_3$ and $\text{SiCl}_4.6\text{NH}_3$, have been shown to be actually mixtures of amide or imide and ammonium chloride, as represented by the equations—



and the zirconium halogen ammonia compounds belong to the same category, as shown by their behaviour towards liquid ammonia. For by washing the iodide compound with liquid ammonia, ammonium iodide can be extracted, and the percentage of zirconium rises from 12 to 45 per cent. The authors have prepared a compound of zirconium iodide and 6 molecules of ethylamine. With ether, ZrI_4 forms yellow, very unstable crystals, which dissolve on addition of excess of ether. These crystals have apparently the composition expressed by the formula

$ZrI_{4.4}(C_2H_5)_2O$, but on account of their instability the analytical results cannot be regarded as very trustworthy.

Titanium.—Arthur Stähler and Heinz Wirthwein.—The authors prepare pure titanium material as follows:—The minerals rutile, titanium iron ore, or yttritanite, are mixed with carbon and fused in the electric furnace, when carbides are formed. These are then treated with dry chlorine, and the titanium tetrachloride can be separated by distillation. In order to obtain it free from vanadium it is shaken for forty-eight hours with a little sodium amalgam till it becomes quite colourless. When rutile is treated directly with sulphur chloride the iron and vanadium escape as chlorides, while nearly pure titanium oxide remains behind; it is, however, slowly converted completely into chloride, which can not be separated from the sulphur chloride by distillation, owing to the close proximity of the boiling-points of the two liquids. The authors find that, contrary to the statements of former investigators, tetravalent titanium is not coloured yellow by pure ether in presence of alcohol. If hydrogen peroxide is present in the ether the reaction occurs; alcohol need not be present. The authors have prepared the following compounds of trivalent titanium:—



When excess of liquid ammonia is allowed to act upon $TiCl_4$, the compound $TiCl_4 \cdot 8NH_3$ is produced as a yellow powder.

MISCELLANEOUS.

Schools of Chemistry, &c.—The following additional information has been received:—

NORTHAMPTON INSTITUTE, St. John Street Road, E.C.—Principal, R. Mullineux Walmsley, D.Sc., F.R.S.E.—This Institute is a Technical, Social, and Recreative Institute for both sexes. It was founded as a branch of the City Polytechnic, and its educational aim is to provide classes in technological and trade subjects. The educational courses fall into two distinct sections:—(a). Day Courses for students who are willing to give the whole of their time for one or more years to a thorough systematic training in one of the technological subjects dealt with; and (b) Evening Courses and Classes for those who are unable to attend during the daytime. Day and Evening Courses in Engineering (Mechanical and Electrical), Technical Optics, in Artistic Crafts, and Horology (commencing Monday, October 2). Evening Courses in Technical Chemistry and Domestic Economy (commencing Monday, September 25).

SIR JOHN CASS TECHNICAL INSTITUTE, Jewry Street, Aldgate.—Established in 1710 as a Foundation School by the generosity of the citizen whose name it bears, after several developments, and as a result of increased revenues, it has now become a popular educational centre, and one of the Polytechnics aided by the London County Council. The new building was formally opened in 1902, and the fourth session will begin on Monday next, the 25th inst. Thoroughly complete laboratories and workshops are provided for instruction in Metallurgy, Assaying, Metal work, Jewellery, Enamelling, Glass-blowing, &c., under an efficient teaching staff, and courses of study are arranged for those engaged in chemical and electrical industries. Classes are also held in other branches of education.

COUNTY BOROUGH OF WEST HAM MUNICIPAL TECHNICAL INSTITUTE, Romford Road, E.—Day Technical Courses in Mechanical, Civil, and Electrical Engineering, Pure and

Applied Chemistry, and Building (commencing October 3), for students who are able to devote their whole time to study, with the aim of giving a sound scientific training for industrial life. Evening Technical Courses in various branches of Science and Industry (commencing September 28). Full particulars may be obtained from the Calendar of the Institute, price 1d. (post free, 3d).

Appointment.—Mr. E. Towyn Jones, B.Sc., Demonstrator in Chemistry at University College, Bangor, has been appointed Assistant-Lecturer and Senior Demonstrator in the Department of Chemistry and Physics of the Pharmaceutical Society of Great Britain.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Pine Tar.—Can any reader give reliable information respecting the commercial value of pine tar on English markets? Also in what industry or industries the product is used.—W. E. L.

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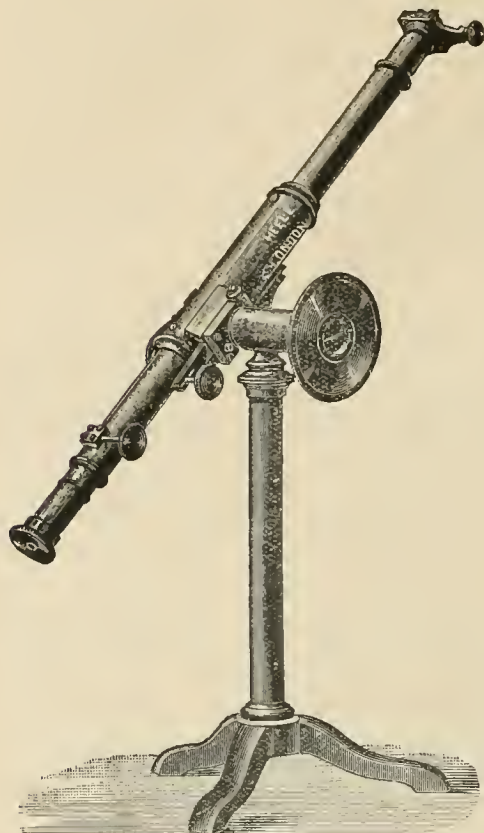
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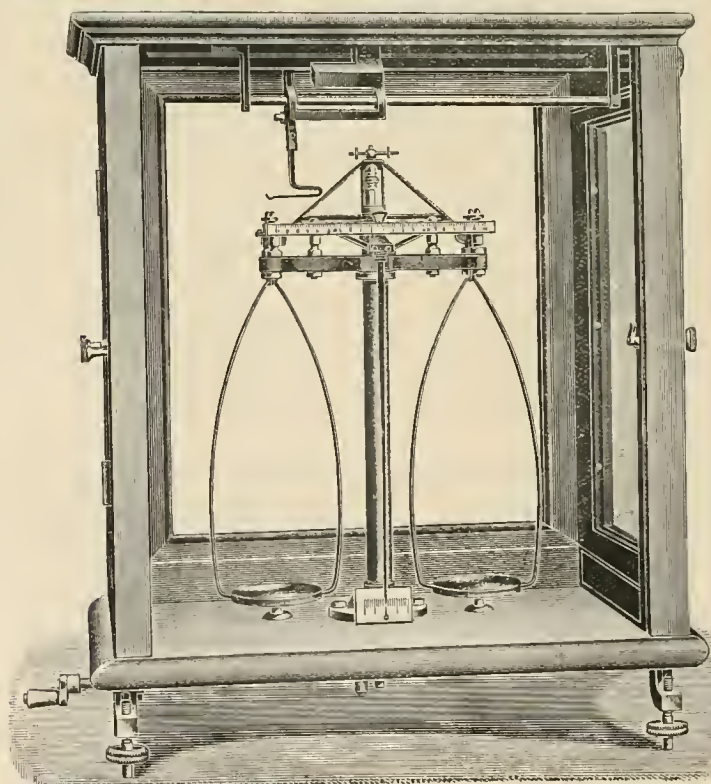
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THE CHEMICAL NEWS.

VOL. XCII., No. 2392.

DIAMONDS.

A LECTURE DELIVERED BEFORE THE BRITISH ASSOCIATION
AT KIMBERLEY, SEPTEMBER 5, 1905.

By Sir WILLIAM CROOKES,
Hon. D.Sc. (Oxford and Dublin), F.R.S.

(Continued from p. 140).

Genesis of the Diamond.

SPECULATIONS as to the probable origin of the diamond have been greatly forwarded by patient research, and particularly by improved means of obtaining high temperatures, an advance we owe principally to the researches of Professor Moissan.

Until recent years carbon was considered absolutely non-volatile and infusible; but the enormous temperatures at the disposal of experimentalists—by the introduction of electricity—show that, instead of breaking rules, carbon obeys the same laws that govern other bodies. It volatilises at the ordinary pressure at a temperature of about $3600^{\circ}\text{C}.$, and passes from the solid to the gaseous state without liquefying. It has been found that other bodies, such as arsenic, which volatilises without liquefying at the ordinary pressure, will easily liquefy if pressure is added to temperature. It naturally follows that if along with the requisite temperature sufficient pressure is applied, liquefaction of carbon will take place, when on cooling it will crystallise, but carbon at high temperatures is a most energetic chemical agent, and if it can get hold of oxygen from the atmosphere or any compound containing it, it will oxidise and fly off in the form of carbonic acid. Heat and pressure therefore are of no avail unless the carbon can be kept inert.

It has long been known that iron when melted dissolves carbon, and on cooling liberates it in the form of graphite. Moissan discovered that several other metals, especially silver, have similar properties; but iron is the best solvent for carbon. The quantity of carbon entering into solution increases with the temperature.

For the manufacture of—I am afraid I must say an infinitesimal—diamond, the first necessity is to select pure iron—free from sulphur, silicon, phosphorus, &c.,—and to pack it in a carbon crucible with pure charcoal from sugar. The crucible is then put into the body of the electric furnace, and a powerful arc formed close above it between carbon poles, utilising a current of 700 amperes at 40 volts pressure. The iron rapidly melts and saturates itself with carbon. After a few minutes heating to a temperature above $4000^{\circ}\text{C}.$ —a temperature at which the iron melts like wax and volatilises in clouds—the current is stopped, and the dazzling fiery crucible is plunged beneath the surface of cold water, where it is held until it sinks below a red heat. As is well known, iron increases in volume at the moment of passing from the liquid to the solid state. The sudden cooling solidifies the outer layer of iron and holds the inner molten mass in a tight grip. The expansion of the inner liquid on solidifying produces an enormous pressure, and under the stress of this pressure the dissolved carbon separates out in transparent forms—minutely microscopic, it is true—all the same veritable diamonds, with crystalline form and appearance, colour, hardness, and action on light the same as the natural gem.

Now commences the tedious part of the process. The metallic ingot is attacked with hot nitro-hydrochloric acid until no more iron is dissolved. The bulky residue consists chiefly of graphite, together with translucent chesnut-coloured flakes of carbon, black opaque carbon of a density of from 3.0 to 3.5 , and hard as diamonds—black diamonds

or carbonado, in fact,—and a small portion of transparent colourless diamonds showing crystalline structure. Besides these, there may be carbide of silicon and corundum, arising from impurities in the materials employed.

The residue is first heated for some hours with strong sulphuric acid at the boiling point, with the cautious addition of powdered nitre. It is then well washed, and for two days allowed to soak in strong hydrofluoric acid in cold, then in boiling acid. After this treatment the soft graphite disappears, and most if not all the silicon compounds have been destroyed. Hot sulphuric acid is again applied to destroy the fluorides, and the residue, well washed, is attacked with a mixture of the strongest nitric acid and powdered potassium chlorate, kept warm—but not above $60^{\circ}\text{C}.$, to avoid explosions. This treatment must be repeated six or eight times, when all the hard graphite will gradually be dissolved, and little else left but graphitic oxide, diamond, and the harder carbonado and boart. The residue is fused for an hour in fluorhydrate of fluoride of potassium, then boiled out in water, and again heated in sulphuric acid. The well washed grains which resist this energetic treatment are dried, carefully deposited on a slide, and examined under the microscope. Along with numerous pieces of black diamond are seen transparent colourless pieces, some amorphous, others with a crystalline appearance. Although many fragments of crystals occur, it is remarkable I have never seen a complete crystal. All appear shattered, as if on being liberated from the intense pressure under which they were formed they burst asunder. I have singular evidence of this phenomenon. A fine piece of artificial diamond, carefully mounted by me on a microscopic slide, exploded during the night and covered the slide with fragments. Moissan's crystals of artificial diamond sometimes broke a few weeks after their preparation, and some of the diamonds which cracked weeks or even months after their preparation showed fissures covered with minute cubes. This bursting paroxysm is not unknown at the Kimberley mines.

On the screen I will project photographs of artificial diamonds manufactured in the manner described. So far, these specimens are all microscopic. The largest artificial diamond is less than one millimetre across.

These laboratory diamonds burn in the air before the blowpipe to carbonic acid. In lustre, crystalline form, optical properties, density, and hardness, they are identical with the natural stone.

In several cases Moissan separated ten to fifteen microscopic diamonds from a single ingot. The larger of these are about 0.75 m.m. long; the octahedra being 0.2 m.m.

Graphite.

Intermediate between soft carbon and diamond come the graphites. The name graphite is given to a variety of carbon, generally crystalline, which in an oxidising mixture of chlorate of potassium and nitric acid forms graphitic oxide. This varies in colour from green to brown or yellow, or it is almost without colour, according to the completeness of the reaction. Graphites are of varying densities, from 2.0 to 3.0 , and generally of crystalline aspect. Graphite and diamond pass insensibly into one another. Hard graphite and soft diamond are near the same specific gravity. The difference appears to be one of pressure at the time of formation.

Some forms of graphite exhibit the remarkable property by which it is possible to ascertain approximately the temperature at which they were formed, or to which they have subsequently been exposed. Sprouting graphite is a form, frequently met with in nature, which on moderate heating swells up to a bulky, very light mass of amorphous carbon. Moissan has found it in blue ground from Kimberley; my own results verify his. When obtained by simple elevation of temperature in the arc or the electric furnace graphites do not sprout; but when they are formed by dissolving carbon in a metal at a high temperature and then allowing the graphite to separate out on cooling, the sprouting variety appears. The phenomenon of sprouting is easily

shown. I place a few grains in a test-tube and heat it to about 170°C. , when you see the grains increase enormously in bulk and fill the tube with a light form of amorphous carbon.

The resistance of a graphite to oxidising agents is greater the higher the temperature to which it has previously been exposed. Graphites which are easily attacked by a mixture of fuming nitric acid and potassium chlorate are rendered more resistant by strong heat in the electric furnace.

Boiling- and Melting-point of Carbon.

On the average the critical-point of a substance is 1.5 times its absolute boiling-point. Therefore the critical-point of carbon should be about 5800°Ab. But the absolute critical temperature divided by the critical pressure is for all the elements so far examined never less than 2.5; this being about the value Sir James Dewar finds for hydrogen. So that, accepting this, we get the maximum critical pressure as follows, viz., 2320 atmospheres:—

$$\frac{5800^{\circ}\text{Ab.}}{\text{CrP}} \div 2.5, \text{ or } \text{CrP} = \frac{5800^{\circ}\text{Ab.}}{2.5}, \text{ or } 2320 \text{ atmospheres.}$$

Carbon and arsenic are the only two elements that have a melting-point above the boiling-point; and among compounds carbonic acid and fluoride of silicon are the only other bodies with similar properties. Now the melting-point of arsenic is about 1.2 times its absolute boiling-point. With carbonic acid and fluoride of silicon the melting-points are about 1.1 times their boiling-points. Applying these ratios to carbon we find that its melting-point would be about 4400° .

Therefore, assuming the following data

Boiling-point	3870°Ab.
Melting-point	4400
Critical temperature . .	5800
Critical pressure	2320 Ats.

the Rankine or Van der Waals formula calculated from the boiling-point and critical data would be as follows:—

$$\log. P = 10.11 - 39120/T,$$

and this gives for a temperature of 4400°Ab. a pressure of 16.6 Ats. as the melting-point pressure. The results of the formula are given in the form of a table:—

Temperature.	Pressure.	
Ab.	Ats.	
3870°	1.00	Boiling-point.
4000	2.14	
4200	6.25	
4400	16.6	Melting-point.
4600	40.4	
4800	91.2	
5000	193	
5200	386	
5400	735	
5600	1330	
5800	2320	Critical-point (15 tons per square inch).

If then we may reason from these rough estimates, above a temperature of 5800°Ab. no amount of pressure will cause carbon vapour to assume liquid form, whilst at 4400°Ab. a pressure of above 17 atmospheres would suffice to liquefy some of it. Between these extremes the curve of vapour pressure is assumed to be logarithmic, as represented in the accompanying diagram. The constant 39120 which occurs in the logarithmic formula enables us to calculate the latent heat of evaporation. If we assume the vapour density to be normal, or the molecule in vapour as C_2 , then the heat of volatilisation of 12 grms. of carbon would be 90,000 calories; or, if the vapour is a condensed molecule like C_6 , then the 12 grms. would need 30,000 calories. In the latter case the evaporation of 1 grm. of carbon would require 2500 calories, whereas a substance like zinc needs only about 400 calories.

A New Formation of Diamond.

I have long speculated as to the possibility of obtaining artificially such pressures and temperatures as would fulfil the above conditions. In their researches on the gases from fired gunpowder and cordite, Sir Frederick Abel and Sir Andrew Noble obtained in closed steel cylinders pressures as great as 95 tons to the square inch, and temperatures as high as 4000°C. According to a paper recently communicated to the Royal Society, Sir Andrew Noble, exploding cordite in closed vessels, has obtained a pressure of 8000 atmospheres, or 50 tons per square inch, with a temperature reaching in all probability 5400°Ab.

Here, then, we have conditions favourable for the liquefaction of carbon, and were the time of explosion sufficient to allow the reactions to take place, we should certainly expect to get the liquid carbon to solidify in the crystalline state.*

By the kindness of Sir Andrew Noble I have been enabled to work upon some of the residues obtained in closed vessels after explosions, and I have submitted them to the same treatment that the granulated iron had gone through. After weeks of patient toil I removed the amorphous carbon, the graphite, the silica,† and other constituents of the ash of cordite, and obtained a residue among which, under the microscope, crystalline particles could be distinguished. Some of these particles, from their crystalline appearance and double refraction, were silicon carbide; others were probably diamonds. The whole residue was dried and fused at a good red heat in an excess of potassium bifluoride, to which was added during fusion 5 per cent of nitre. (Previous experiments had shown me that this mixture readily attacked and dissolved silicon carbide; unfortunately it also attacks diamond to a slight degree). The residue, after thorough washing and then heating in fuming sulphuric acid, was washed, dried, and the largest crystalline particles picked out and mounted. All the operations of washing and acid treatment were performed in a large platinum crucible by decantation (except the preliminary attack with nitric acid and potassium chlorate, when a hard glass vessel was used); the final result was washed into a shallow watch-glass and the selection made under the microscope.

I project on the screen a few photographs of these crystals. From the treatment they have undergone, chemists will agree with me that diamonds only could stand such an ordeal; on submitting them to skilled crystallographic authorities my opinion is confirmed. Speaking of the one before you (303), Professor Bonney calls it "a diamond showing octahedral planes with dark boundaries due to high refracting index." After careful examination, Professor Miers writes of the same crystal diamond:—"I think one may safely say that the position and angles of its faces, and of its cleavages, the absence of birefringence, and the high refractive index, are all compatible with the properties of the diamond crystallising in the form of an octahedron. Others of the remaining crystals, which show a similar high refractive index, appeared to me to present the same features."

It would have been more conclusive had I been able to get further evidence as to the density and hardness of the crystals; but I am still working at the subject, and hope to add these confirmatory tests. From what I have already said I think there is no doubt that in these closed vessel

* Sir James Dewar, in a Friday Evening Discourse at the Royal Institution, 1880, showed an experiment proving that the temperature of the interior of a carbon tube heated by an outside electric arc was higher than that of the oxy-hydrogen flame. He placed a few small crystals of diamond in the carbon tube, and, maintaining a current of hydrogen to prevent oxidation, raised the temperature of the tube in an electric furnace to that of the arc. In a few minutes the diamond was transformed into graphite. At first sight this would seem to show that diamond cannot be formed at temperatures above that of the arc. It is probable, however, for reasons given above, that at exceedingly high pressures the result would be different.

† The silica was in the form of spheres, perfectly shaped and transparent, mostly colourless, but among them several of a ruby colour. When 5 per cent of silica was added to cordite, the residue of the closed vessel explosion contained a much larger quantity of these spheres.

explosions we have another method of producing the diamond artificially.

Sensational as is the story of the diamond industry in South Africa, quite another aspect fixes the attention of the chemist. The diamonds come out of the mines, but how did they get in? How were they formed? What is their origin?

Gardner Williams, who knows more about diamonds than any man living, is little inclined to indulge in specula-

tion. In his fascinating book he frankly says ("The Diamond Mines of South Africa," p. 510; Macmillans, 1902):—

"I have been frequently asked, 'What is your theory of the original crystallisation of the diamond?' and the answer has always been, 'I have none; for after seventeen years of thoughtful study, coupled with practical research, I find that it is easier to "drive a coach and four" through most theories that have been propounded than to suggest one

which would be based on any non-assailable data.' All that can be said is that in some unknown manner carbon, which existed deep down in the internal regions of the earth, was changed from its black and uninviting appearance to the most beautiful gem which ever saw the light of day."

Meteoritic Diamonds.

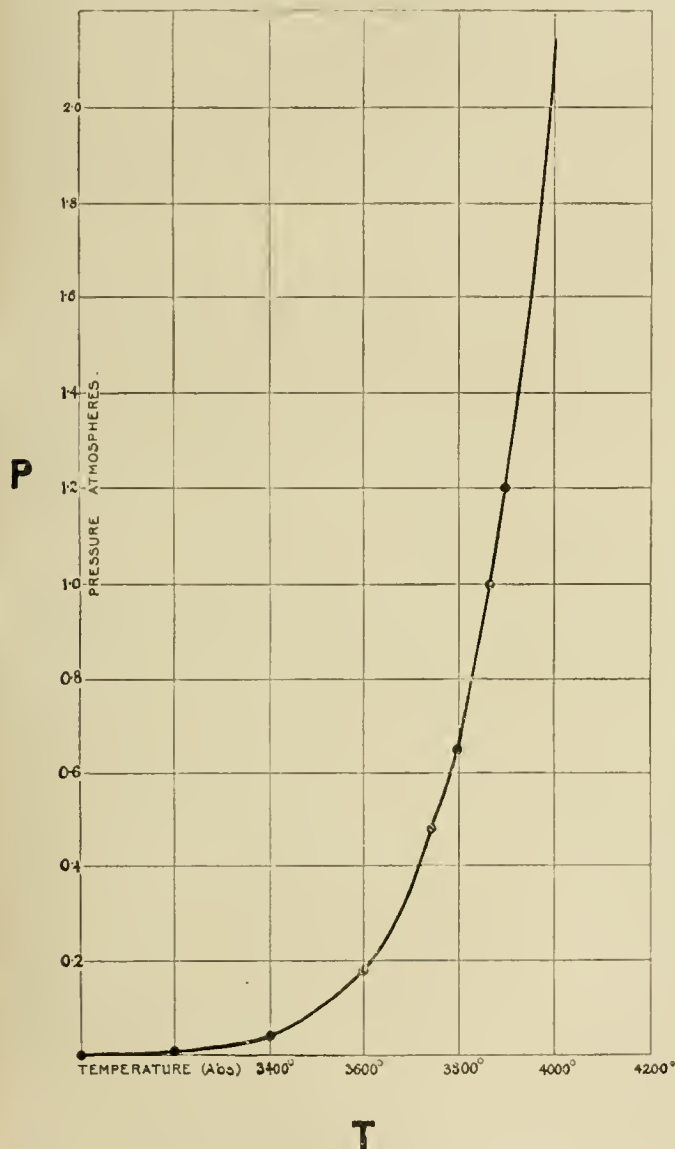
Another diamond theory appeals to the fancy. It is said the diamond is a gift from Heaven, conveyed to earth in meteoric showers. The suggestion, I believe, was first broached by A. Meydenbauer, who says (CHEMICAL NEWS, 1890, vol. lxi., p. 209):—"The diamond can only be of cosmic origin, having fallen as a meteorite at later periods of the earth's formation. The available localities of the diamond contain the residues of not very compact meteoric masses which may, perhaps, have fallen in prehistoric ages, and which have penetrated more or less deeply, according to the more or less resistant character of the surface where they fell. Their remains are crumbling away on exposure to the air and sun, and the rain has long ago washed away all prominent masses. The enclosed diamonds have remained scattered in the river beds, while the fine light matrix has been swept away."

According to this hypothesis, the so-called volcanic pipes are simply holes bored in the solid earth by the impact of monstrous meteors—the larger masses boring the holes, while the smaller masses, disintegrating in their fall, distributed diamonds broadcast. Bizarre as such a theory appears, I am bound to say there are many circumstances which show that the notion of the Heavens raining diamonds is not impossible.

The most striking confirmation of the meteoric theory comes from Arizona. Here, on a broad open plain, over an area about five miles in diameter, have been scattered one or two thousand masses of metallic iron, the fragments varying in weight from half a ton to a fraction of an ounce. There is little doubt these masses formed part of a meteoric shower, although no record exists as to when the fall took place. Curiously enough, near the centre, where most of the meteorites have been found, is a crater with raised edges three-quarters of a mile in diameter and about 600 feet deep, bearing exactly the appearance which would be produced had a mighty mass of iron struck the ground and buried itself deep under the surface. Altogether ten tons of this iron have been collected, and specimens of the Canyon Diablo meteorite are in most collectors' cabinets.

An ardent mineralogist—the late Dr. Foote—cutting a section of this meteorite, found the tools were injured by something vastly harder than metallic iron. He examined the specimen chemically, and soon after announced to the scientific world that the Canyon Diablo meteorite contained black and transparent diamonds. This startling

discovery was afterwards verified by Professors Moissan and Friedel, and Moissan working on 183 kilogrammes of the Canyon Diablo meteorite, has recently found smooth black diamonds and transparent diamonds in the form of octahedra with rounded edges, together with green hexagonal crystals of carbon silicide. The presence of carbon silicide in the meteorite shows that it must, at some time, have experienced the temperature of the electric furnace. Since this revelation, the search for



tion. In his fascinating book he frankly says ("The Diamond Mines of South Africa," p. 510; Macmillans, 1902):—

"I have been frequently asked, 'What is your theory of the original crystallisation of the diamond?' and the answer has always been, 'I have none; for after seventeen years of thoughtful study, coupled with practical research, I find that it is easier to "drive a coach and four" through most theories that have been propounded than to suggest one

diamonds in meteorites has occupied the attention of chemists all over the world.

I am enabled to show you photographs of true diamonds I myself have extracted from the Canyon Diablo meteorite. A fine slab of the meteorite, weighing about seven pounds, is on the table before you.

Here, then, we have incontestible proof of the truth of the meteoric theory. Under atmospheric influences the iron would rapidly oxidise and rust away, colouring the adjacent soil with red oxide of iron. The meteoric diamonds would be unaffected, and left on the surface of the soil, to be found haphazard when oxidation had removed the last proof of their celestial origin. That there are still lumps of iron left at Arizona is merely due to the extreme dryness of the climate and the comparatively short time that the iron has been on our planet. We are here witnesses to the course of an event which may have happened in geologic times anywhere on the earth's surface.

Although in Arizona diamonds have fallen from the skies, confounding our senses, this descent of precious stones is what may be called a freak of Nature rather than a normal occurrence. To the modern student of science there is no great difference between the composition of our earth and that of extra-terrestrial masses. The mineral peridot is a constant extra-terrestrial visitor, present in most meteorites. And yet no one doubts that peridot is also a true constituent of rocks formed on this earth. The spectroscope reveals that the elementary composition of the stars and the earth are pretty much the same; and the spectroscope also shows that meteorites have as much of earth as of heaven in their composition. Indeed, not only are the selfsame elements present in meteorites, but they are combined in the same way to form the same minerals as in the crust of the earth.

It is certain from observations I have made, corroborated by experience gained in the laboratory, that iron at a high temperature and under great pressure—conditions existent at great depths below the surface of the earth—acts as the long-sought solvent for carbon, and will allow it to crystallise out in the form of diamond. But it is also certain, from the evidence afforded by the Arizona and other meteorites, that similar conditions have existed among bodies in space, and that on more than one occasion a meteorite freighted with jewels has fallen as a star from the sky.

Many circumstances point to the conclusion that the diamond of the chemist and the diamond of the mine are strangely akin as to origin. It is evident that the diamond has not been formed *in situ* in the blue ground. The genesis must have taken place at vast depths under enormous pressure. The explosion of large diamonds on coming to the surface shows extreme tension. More diamonds are found in fragments and splinters than in perfect crystals; and it is noteworthy that although these splinters and fragments must be derived from the breaking up of a large crystal, yet in only one instance have pieces been found which could be fitted together, and these occurred at different levels. Does not this fact point to the conclusion that the blue ground is not their true matrix? Nature does not make fragments of crystals. As the edges of the crystals are still sharp and unabraded, the *locus* of formation cannot have been very distant from the present sites. There were probably many sites of crystallisation differing in place and time, or we should not see such distinctive characters in the gems from different mines, nor indeed in the diamonds from different parts of the same mine.

It is not difficult to imagine that masses of iron saturated with carbon existed formerly at a sufficient depth below the present mines, where temperature and pressure would produce the reactions which laboratory experiments show to be probable.

(To be continued).

THE RATE OF OXIDATION IN GASEOUS OXYGEN.

By W. P. JORISSEN and W. E. RINGER.

1. As is well known, the hypothesis of van't Hoff (*Zeit. f. Phys. Chem.*, 1895, xvi., 411; see also Ewan's translation of van't Hoff-Cohen's "Studien zur Chemischen Dynamik," 1896) concerning the activation of oxygen stands in connection with the results of Ewan's experiments on the rate of oxidation in dried oxygen (see also Jorissen, *Zeit. f. Phys. Chem.*, 1897, xxii., 34, 47; 1897, xxiii., 667; *Ber.*, 1896, xxix., 1707; 1897, xxx., 1952; *Arch. Néerl.*, 1897), viz., the proportionality of this rate with the square root of the pressure of the oxygen (*Phil. Mag.*, 1894, [5], xxxviii., 512; *Zeit. f. Phys. Chem.*, 1895, xvi., 317). This hypothesis, however, was somewhat obscured by that of Bach (*Monit. Scientif.*, July, 1897; J. W. Mellor, "Chem. Statics and Dynamics," 1904, 314) and Engler (Engler and Wild, *Ber.*, 1897, xxx., 1674; Engler and Weissberg, "Kritische Studien über die Vorgänge der Autoxydation," 1904).

Several phenomena, however, which accompany the oxidation of phosphorus have again brought it forward, though in a somewhat changed shape. (See paper by W. P. Jorissen, *CHEMICAL NEWS*, xcii., 62).

In connection with this revival, the controlling of the result obtained by Ewan is desirable. For this it will be best to study the case of a homogeneous mixture of oxygen and a gaseous spontaneously oxidising substance (autoxidiser), the product of oxidation being also gaseous. The oxidation of acetaldehyde, studied by Ewan, nearly represents this case, but the acetic acid which is formed soon condenses and then acts as a solvent for the aldehyde, thus giving rise to a complication.

If the autoxidiser is a liquid (for instance, benzaldehyde, Jorissen, *Chem. Weekblad.*, 1904, i., 803) or a solid (phosphorus and sulphur, Ewan, *loc. cit.*) the influence of the rate of evaporation and of diffusion comes forward.

Nernst and Brunner have drawn the attention to the fact that, in many cases of heterogeneous reactions, the velocity which is measured is only a velocity of diffusion and not the velocity of the reaction (*Zeit. f. Phys. Chem.* 1904, xlvii., 52, 55; see also J. W. Mellor, "Chem. Statics and Dynamics," 1904, 125—140).

Ewan took the influence of the rate of evaporation of the autoxidiser into account, and supposes that the oxidation takes place in the very neighbourhood of the autoxidiser if the pressure of the oxygen is not too small.

But the question remains: is the rate of oxidation greater or smaller than the rate of evaporation? And this rate of evaporation depends again on the size and nature of the surface of the substance.

A very interesting phenomenon in the dominion of the oxidation processes is the so-called "boundary-pressure" (see *f.i.* Mellor, *loc. cit.*, pp. 417—428, 440—443). This pressure has been studied best for the oxidation of phosphorus (Joubert, Ewan, Centnerszwer, E. J. Russell). Joubert found indications for this limit in the case of sulphur and arsenic (*Thèses*, 1874, 16—17). Ewan also has presumptions as regards sulphur, and his experiments made the existence of a limiting-pressure in the case of acetaldehyde probable.

It remains to be said that the rate of oxidation of a few substances (see Mellor, *loc. cit.*, p. 442), for instance, phosphine (Houton de Labillardière, van't Hoff, "Etudes," 1834, 60—67; Van de Stadt, *Zeit. f. Phys. Chem.*, 1893, xii., 322), is accelerated by diminishing the pressure. In very few cases only the existence of a boundary-pressure has been investigated. In the case of nickel carbonyl the spontaneous inflammability was still observed at a pressure of 13 atmospheres (Reicher and Jorissen, *Maandbl. v. Natuurwetensch.*, 1894, No. 1), while the oxidation of benzaldehyde in not dried oxygen still takes place in the dark at a pressure of 8.2 atmospheres (Jorissen, *Chem. Weekblad.*, 1904, i., 805).

Morphine may be used for detecting formaldehyde, and, inversely, formaldehyde detects morphine and its derivatives. —*Chemist and Druggist*.

2. The method, used by Joubert (Thèses, Paris, 1874) in his experiments on the boundary pressure in the case of phosphorus, consisted in the determination at a given temperature of the pressure at which the glow appeared. He made use of pure oxygen (does not speak, however, of drying this gas), and let it enter into the evacuated apparatus, which was connected with an open mercury manometer as described by Regnault. After making his eyes sensitive by remaining in the dark for some time, he let the mercury flow out till the glow became perceptible. Then he increased the pressure till the glow disappeared, let the mercury flow out again, &c. The average of six observations (at one and the same temperature), which differed 10 to 15 m.m., he accepted as the boundary-pressure. The experiments made at the same temperature with oxygen and phosphorus of different preparations gave large differences between them. Thus he found, for instance, in two series:—

11°5'	580 m.m.	11°0'	495 m.m.
14°2'	650 "	15°2'	570 "
18°0'	730 "	16°0'	595 "
19°2'	760 "		

He confesses that he does not feel sure to what cause he must ascribe this, and does not seem to have considered the possible influence of moisture.

Ewan (*loc. cit.*), who traced the oxidation of phosphorus by looking for a change of the manometer at a given pressure and temperature, mentions that in wet oxygen at a temperature of 20°4' to 20°7' no oxidation was to be observed at a pressure of 695·6 m.m. in twenty-two minutes; it was observed, however, after fifty minutes. At a temperature of 20°43' to 20°64' no oxidation took place at a pressure of 722·8 m.m. in fifty-two minutes, while it became perceptible at a pressure of 671·1 m.m. in forty-three minutes.

In using oxygen dried by means of phosphorus pentoxide at a temperature of 20°87' to 21°26' no oxidation was observed at a pressure of 377·0 m.m. (after seventy minutes), while again perceptible at a pressure of 201·6 m.m. (after one hundred and ten minutes).

Centnerszwer mentions as the boundary pressure in wet oxygen at 20° 367 m.m. (*Zeit. f. Phys. Chem.*, 1898, xxvi., 21). Just like Joubert, he observed the pressure at which the phosphorus began to become luminous while diminishing the pressure by means of an air-pump. The more slowly he evacuated the higher the pressure was found to be at which a glowing was perceptible. The observations, however, gave differences of 50 m.m. As a rule, the diminishing of the pressure till this point was reached, took forty-five to sixty minutes, and in this way he made observations which agreed sufficiently well with each other. As, however, he describes an intermittent phosphorescence which took place at a pressure 50 m.m. above the glow pressure, the latter must be much lower than the real boundary pressure.

E. J. Russell (*Journ. Chem. Soc.*, December, 1903, p. 1279) did not observe an oxidation of phosphorus in wet oxygen under high pressures even after six months; however, he did not find a boundary pressure in oxygen dried by sulphuric acid.

As Ewan observed such a pressure in oxygen dried by phosphorus pentoxide, and Brereton Baker* could not observe an oxidation of phosphorus at all in oxygen dried for a long time by this substance, this behaviour of sulphuric acid as a drying agent would appear strange.

Now, Russell let the oxygen, prepared by heating pure chlorate or permanganate of potassium, enter the apparatus, in which the phosphorus was present, without taking care to exclude possible traces of ozone† or oxygen ions.

Therefore when undertaking to study the boundary pressure of oxygen, we came to the conclusion that it would be necessary to prepare the oxygen beforehand, and only to use it after waiting for some days, washing it by means of solutions of potassium iodide and caustic potash, and drying it by chloride of calcium.

We also chose as a method of observation that of Ewan, viz., the manometric, and used as a liquid for the manometer either water or water-free glycerin.

The apparatus consisted in a vessel of about 100 c.m.³, provided with a supply tube with tap, so that oxygen could be passed through. The vessel was closed by a ground hollow stopper, to which a thin test-tube was soldered. This test-tube was covered by a layer of pure phosphorus, which could be kept cold by a stream of water flowing through the tube, and of the same temperature (15°) as the water which filled the thermostat. In this thermostat, which was kept at a constant temperature by means of a toluol regulator, the vessel and a flask, which will be described presently, were immersed. To the vessel was also soldered a tube which led to a manometer with water or glycerin, and also to the above-mentioned flask. This flask, partly filled with mercury, was closed by a cork soaked with paraffin and covered with sealing-wax, through which passed four tubes. One of these tubes connected the flask with the vessel, the second with a mercury manometer, the third with a mercury syphon which enabled us to increase or to decrease the pressure in the flask (and the vessel) slowly or quickly. The fourth tube served as a gas abduction tube, and was provided with a tap. The results are briefly communicated below.

Oxygen* Saturated with Water-vapour, Temperature 15° C.

Experiment 1.—No oxidation perceptible at a pressure of 633 m.m. (twenty minutes), which was, however, to be observed at 604 m.m. (32 m.m. of water in sixteen minutes).

Experiment 2.—No oxidation at a pressure of 628 m.m. (seventeen minutes), oxidation at 598 m.m. (27 m.m. of water in forty minutes).

At Experiment 2 a retardation was observed at the beginning. Even at a pressure of 525 m.m. no oxidation took place (seven minutes); it did, however, take place at 508 m.m. (33 m.m. of water in seven minutes). On our increasing the pressure to 628 m.m. the oxidation stopped.

At Experiment 1, where the oxidation took place at a pressure of 604 m.m., we increased the pressure after sixteen minutes to 623 m.m. The oxidation, however, did not stop; after eight minutes the pressure was increased to 634 m.m.—still the oxidation went on. After eighteen minutes, the pressure being increased to 648 m.m., the same took place; also when after thirty-four minutes the pressure was brought as high as 680 m.m. At this pressure, however, the oxidation went on very slowly (8 m.m. of water in twenty-nine minutes). The layer of phosphorus was not the same in Experiments 1 and 2.

With the layer of Experiment 1 a large number of experiments were made. Between each series of experiments the phosphorus was kept in the dark submersed in water.

During these observations some c.c. of a 10 per cent solution of potassium iodide were present in the vessel in order to absorb the ozone which might be formed.

The following retardations were now observed:—

- a. No oxidation at 520 m.m. (25 minutes), but at 512 m.m.
- b. " 592 " (34 "), " 527 "
- c. " 525 " (26 "), " 476 "
- d. " 513 " (10 "), " 495 "
- e. " 514 " (10 "), neither at 481·5 m.m. (5 minutes), but at 464 m.m.

The oxidation having once begun, the pressure was

* *Phil. Trans.*, 1888, 571. He says:—"The pressure was varied in every possible way," but it does not seem to be sure that he experimented at very low pressures.

† For the influence of traces of ozone see Chappuis, *Bull. Soc. Chim. de Paris*, 1881, xxxv., 419.

* The oxygen contained in Experiment 1 4·3 per cent, in Experiment 2 4·2 per cent of nitrogen, determined after having made the oxygen pass through the apparatus for a long time. The pressure of the oxygen was corrected by means of the result of this analysis. According to Centnerszwer 5 per cent of nitrogen would lower the boundary pressure with 13 m.m.

quickly increased to about 633 m.m., at which pressure the oxidation soon ceased. After that the pressure was again lowered. If oxidation took place it was again stopped by increasing the pressure to 633 m.m., &c. As a rule no further retardation was found during such a series of observations.

We were now able to enclose the boundary pressure between two limits* :—

No oxidation.	Oxidation.
626 m.m. (45 mins.)	593 (7 m.m. of water in 22 mins.)
601 " (78 ")	591 (27 " " 80 ")
637 " (39 ")	602 (7.5 " " 26 ")
604 " (40 ")	

The pressures at which oxidation took place in presence of a solution of potassium iodide were practically found to be the same as those observed in the experiments when only water was present.†

In round figures the boundary pressure can be fixed at 600 m.m. at a temperature of 15°.

Oxygen Dried beforehand by means of Calcium Chloride.—In the vessel, calcium chloride and caustic soda; in the manometer, glycerin was used. At 738 m.m. no oxidation was perceptible in fifteen hours, at 638 and 609 m.m. practically no oxidation either (respectively after three and two hours); at 592 m.m. in fourteen hours a decrease of pressure of about 1.5 m.m. of mercury was observed; at 534 m.m. in six hours a decrease of about 2 m.m. of mercury.

Oxygen Dried beforehand by means of Calcium Chloride.—In the vessel, sulphuric acid; in the manometer, glycerin was used. In order to dry the phosphorus the drops of water were taken away from its surface by means of blotting-paper, and then it was put for some time in an atmosphere of carbon dioxide, dried by means of calcium chloride. On bringing the phosphorus in the vessel it was for a short time exposed to the ordinary air, and so it was impossible to prevent some oxidation taking place. The rate of this oxidation, which went on in the vessel, could be traced by means of the glycerin manometer, and in that way it was found that the rate decreased gradually. For instance, in the first seventeen minutes the absorption corresponded with 40 m.m. of glycerin, but thereupon in fourteen minutes with 22 m.m. After eighteen hours the rate was only 5 m.m. of glycerin in forty minutes; in the next twenty-four hours the pressure diminished with about 1 m.m. of mercury. After waiting again for forty-eight hours it was observed that during the last twenty hours the pressure had not changed at all.

The pressure of the oxygen at that moment was 725 m.m.‡ On diminishing the pressure to 678 m.m. (eighty minutes), 631 m.m. (fifty-five minutes), 634 m.m. (two hundred and sixty minutes), and 585 m.m. (fifty-five minutes) no oxidation was perceptible at all. When, however, the pressure was decreased to 538 m.m. a very slow oxidation was observed, during which, in seventeen hours, a quantity of oxygen was absorbed corresponding with about 4 m.m. of mercury.

On increasing the pressure again to 728 m.m. the oxidation stopped.

After some days the pressure was lowered to 526 m.m. Again oxidation took place; in sixteen hours a diminution of the pressure of about 6 m.m. of mercury was observed.

Oxygen Dried beforehand by Phosphorus Pentoxide.—In the vessel, phosphorus pentoxide; in the manometer, glycerin was used. Also in this case some oxidation was observed in the beginning of the experiments, but it stopped much sooner than in the case of sulphuric acid being used.

From a large number of experiments, made under these

circumstances, we quote that at 445 m.m. no oxidation was perceptible after eleven hours, and that the highest pressure at which an oxidation could be observed with certainty was 330 m.m. (about 0.5 m.m. of mercury in 1.75 hours, after that about 1.5 m.m. in 2.5 hours).

These experiments will be repeated with different mixtures of sulphuric acid and water in the vessel; thus in oxygen with water-vapour of different pressures. As to the influence of different radiations, we only state that 5 m.grms. of pure radium bromide (manufactured by Dr. Richard Sthamer, Hamburg) appeared to have no perceptible influence. The oxygen was exposed in this experiment to the influence of this substance in exactly the same way as was the case in our experiments (*Ber.*, 1905, xxxviii., 899) on the influence of radium rays on a mixture of hydrogen and chlorine, which gave a positive result. An influence of the light of an electric arc on the boundary pressure was observed, however. The thermal radiations were kept back as much as possible by means of a small vessel filled with water, while the bundle of light must also penetrate the layer of water in the thermostat.

Whereas the decrease of pressure in the dark was 6.5 m.m. of water in sixty-eight minutes (the pressure thus being very near to the boundary pressure); this decrease amounted to 116 m.m. of water in one hundred and three minutes after the light was put on.

When the light was extinguished it was found to be 60 m.m. of water in forty-eight minutes. The rate of oxidation, therefore, still increased after the light being extinguished.

Of more importance will be to study the action of ultra-violet rays obtained, for instance, by the uvioi-lamp of Messrs. Schott and Co., at Jena; that is, if the oxidation vessel is made of the same glass as that of the uvioi-lamp. These experiments are in a state of preparation.

Helder, Holland, June, 1905.

THE DETECTION OF METHYL ALCOHOL.*

By HEYWARD SCUDDER.

(Concluded from p. 141).

Reagent, Resorcin.

Mulliken-Scudder Test (*Ann. Chem. Journ.*, 1899, xxi., 266).—In its simplest form this consists in oxidising a dilute solution of the alcohol by plunging into it several times a spiral of copper wire heated to redness. The formaldehyde formed is tested for by adding one drop of a 0.5 per cent aqueous solution of resorcin, and pouring, without mixing, on top of a little concentrated sulphuric acid in a test-tube. A contact ring and, on very gentle shaking, flocks of a characteristic red colour appear, if formaldehyde is present. Acetaldehyde gives a ring and flocks of a colour that varies from yellow to brown. This shows 8 to 10 per cent of methyl alcohol in ethyl. The time required is about five minutes.

The modified form is more delicate (Mulliken, Scudder, *Ibid.*, 1900, xxiv., 444). The oxidation is carried out in the same way, but the acetaldehyde is removed by boiling the solution down about one-half. This may be done over a free flame for rapid work. In boiling down, some formaldehyde is always lost, and the more rapid the boiling the greater the loss. Therefore, it is advisable to boil down at 25–30 under diminished pressure in order to get the best results. Where little formaldehyde is present the formation of flocks is slow, so in this modified form after the solution is brought in contact with the sulphuric acid it must be allowed to stand for three minutes, then shaken very gently for a minute, causing the two liquid surfaces in contact to mix, but not allowing rapid or

* Presented before the New York Section of the American Chemical Society. From the *Journal of the American Chemical Society*, July, 1905.

* Percentage of nitrogen respectively 3.27, 3.27, 3.9, and 3.0.

† The fact that a solution of potassium iodide, which is indeed a destroyer of ozone, does not affect the boundary pressure, is important in connection with the opinion of Schönbein, Centnerszwer, and Bödlander, who point out that several of the substances which have considerable influence are known destroyers of ozone.

‡ Corrected for 5.4 per cent of nitrogen.

excessive mixing. If only a very little formaldehyde is present, rapid mixing prevents the formation of flocks, although it has little or no bad effect when much formaldehyde is present. The formation of flocks is a necessary part of the test, a contact ring of the proper colour not being considered sufficient evidence, since acetone and dimethyl-ethylcarbinol both give red contact rings. Methyl esters and ethers, methylal, and secondary and tertiary butyl alcohols give the same reaction as methyl alcohol in this test. This would indicate that whenever a methyl group and oxygen are close together and not bound firmly to the remainder of a compound, oxidation may produce formaldehyde, the amount formed probably being dependent on the relative attraction between the different groups in the compound. This test shows 2 to 3 per cent methyl alcohol in ethyl. The time required is about twenty minutes. One great advantage of the test is that the formation of flocks of characteristic colour gives a very positive indication, much more so than the production of a contact ring or of a temporary colour.

United States Pharmacopœia Test.—Sadler states that the committee for the revision of the Pharmacopœia found resorcin more delicate than phloroglucin as a test for the formaldehyde produced in the oxidation of methyl alcohol (*Am. Journ. Pharm.*, 1905, lxxvii., 106). They give the following directions:—Ten c.c. of the solution to be tested, having a concentration of about 10 per cent (in testing liquors or alcohol, the proper dilution must be made), are placed in a test-tube surrounded by cold water. It is oxidised by plunging a red-hot spiral of copper wire—of specified dimensions—to the bottom of the test-tube and holding it there one to two seconds. This is repeated five to six times. The filtered solution is boiled gently till any odour of acetaldehyde ceases to be clearly distinguishable. To the cooled solution one drop of a 1 : 200 aqueous solution of resorcin is added, and the mixture is floated on top of concentrated sulphuric acid in a test-tube. After standing three minutes the tube is gently rotated. If no rose-red ring appears, less than 2 per cent of methyl alcohol is present. The time required for the test is about fifteen minutes.*

Mulliken Test ("Provisional Methods for Analysis of Foods," U.S. Dept. Agriculture, Bureau Chemistry, *Bull.* 65, 73, 1902).—The alcohol is oxidised by a heated copper spiral, ammonia is then added, and the solution is boiled gently in a dish till the odour of ammonia has disappeared. The acetaldehyde is thus driven off and the formaldehyde is converted into hexamethylenetetramine. Concentrated hydrochloric acid is then added, and the solution brought momentarily to boiling to decompose the hexamethylenetetramine. The formaldehyde set free is tested for by resorcin as in the Mulliken-Scudder test. The test shows 10 per cent methyl alcohol in ethyl, and an expert is said to be able to detect less than this amount.

This test is no more delicate than the simple form of the Mulliken-Scudder test, so that its advantage is not apparent. Theoretically, the method is one that promises well. Ammonia unites with formaldehyde very rapidly to form hexamethylenetetramine, a compound that is stable on boiling, and does not distil off to any extent, while acetaldehyde-ammonia is decomposed by heat, and the acetaldehyde can be completely driven off by boiling. There are two defects in the process that I have not been able to overcome in any way. The addition of ammonia retains all the formaldehyde produced in the oxidation of ethyl alcohol, so that any delicate test applied after the decomposition of the hexamethylenetetramine, whether the test is for the formaldehyde or for the ammonia, is given both by ethyl and methyl alcohol. The oxidation

by a copper spiral does not produce enough formaldehyde from methyl alcohol to allow as a test the use of the formation of some compound of hexamethylenetetramine, such as the tetraiodide or the mercuric chloride compound, although both these compounds (which give difficultly soluble precipitates) can be used to detect the presence of quite small quantities of hexamethylenetetramine. No precipitate is formed from quantities of hexamethylenetetramine sufficient to give, after decomposition by boiling with acid, fairly thick flocks in the resorcin test. In this decomposition some formaldehyde is always lost, since other compounds besides ammonia and formaldehyde are formed. It is advisable to boil for fifteen or twenty seconds or longer to get the maximum amount of formaldehyde.

Reagent, Fuchsin.

Another use of hexamethylenetetramine gave promise, but fails at times for reasons that I cannot discover. The solution is oxidised by a heated copper spiral, filtered, an excess of ammonia added, and then boiled down about two-thirds. It is then cooled and 2 c.c. of fuchsin aldehyde reagent added. The sulphurous acid in this decomposes the hexamethylenetetramine and the aldehyde set free instantly colours the solution. A blank of pure water and fuchsin reagent is made, and the difference in colour and the time noted. In this way it was possible to show 1 per cent methyl alcohol in ethyl in fifteen minutes. But at times pure ethyl alcohol would give a colour as deep and as rapidly formed as that from methyl alcohol. As a rule ethyl alcohol when oxidised gives a colour that is very faint at first, and does not deepen for so long a time that the distinction between it and that from methyl alcohol is sufficiently marked to make a good test.

Reagent, Phloroglucin.

Acetaldehyde in amounts less than 0.01 per cent gives no reaction with an alkaline solution of phloroglucin in the Haigh and the Prescott tests, but will give a reaction with 1.0 c.c. or 2.5 c.c. of alkaline phloroglucin as used in the Sanglé-Ferrière test. In large quantities—over 0.1 per cent—it will also give a colour with the phloroglucin solution in the Haigh test. Formaldehyde in very small amounts gives a colour permanent for several minutes. The colour is said to be pure red. Actually it depends on the relative concentrations of the formaldehyde and the phloroglucin, varying from yellowish red through pure red to violet-red. Since, in any solution to be tested, the quantity of methyl alcohol present may be anywhere from 1 per cent to 100 per cent, oxidation will produce a very variable amount of formaldehyde, but the conditions of any test call for a fixed amount of phloroglucin; so the colour may be pure red or may be any of the shades mentioned.

Sufficient formaldehyde is formed in the oxidation of ethyl alcohol to give a colour with phloroglucin, though this colour is fainter than that obtained from the oxidation of solutions containing over 10 per cent of methyl alcohol. The colour is said to differ in quality from that obtained from oxidised methyl alcohol. I have not found this statement to be true, for the reason just given.

The colour obtained from oxidised methyl alcohol is said to be much more permanent than that given by oxidised ethyl alcohol. While this is true, the colour given by ethyl alcohol often lasts for a number of minutes, so that it is impossible to distinguish between ethyl and methyl alcohol either by this criterion or by the difference in colour, without making a comparative test with ethyl alcohol. In some experiments on the duration of the colour (the oxidant was a heated copper spiral), a 10 per cent aqueous solution of methyl alcohol gave a red that lasted for ten minutes without any noticeable fading; then it gradually grew lighter. At the end of twenty minutes the colour was still well marked. At the end of one hour there was no colour. A 20 per cent aqueous solution of ethyl alcohol gave a distinct red that lasted for six minutes, then began to fade. At the end of fifteen minutes the colour was very faint. A 20 per cent aqueous solution of a mixture of

* When I read this paper, I gave the outlines of a rapid test that would show 2 per cent methyl alcohol in ethyl. Since that time Sadler has published the test just given. The procedure of my test differed in several points, but the two are so much alike that it seems inadvisable to burden the literature with the details of mine. The fact that with such differences in procedure the results obtained are the same, shows that the Pharmacopœia test can be recommended to persons of limited chemical experience.

2 parts methyl alcohol and 98 parts ethyl alcohol, boiled down one-half after oxidation, gave a red that was deep for one minute, then faded, but was noticeable for more than ten minutes. A 20 per cent solution of ethyl alcohol similarly treated gave a colour that faded from the beginning and was hardly noticeable after three minutes.

The full depth of colour is sometimes not reached for one to two minutes. The duration of the colour is lessened by stirring.

When the solution is boiled, the colour changes to a clear brown-yellow. This same colour develops on boiling solutions that have become colourless. When cooled, after boiling, the colour from methyl alcohol is permanent for one to two minutes, then fades more or less slowly, while the colour from ethyl alcohol becomes very faint or disappears as soon as the solution is cold. This disappearance or fading of colour in the case of ethyl alcohol is noticed with certainty only when an excess of alkali is added, since the phloroglucin solution as ordinarily prepared will give, after boiling, a faint violet in the cold. The excess of alkali destroys this violet colour. When there is doubt as to the presence of methyl alcohol, on account of the faint or transient colour obtained by the ordinary test with phloroglucin in the cold, the question can often be settled definitely by the addition of an excess of alkali, boiling, and noting the depth and permanence of the colour of the cold solution.

Whenever phloroglucin is used as the agent to detect formaldehyde in testing for methyl alcohol, a comparative test with pure ethyl alcohol must always be made, since it is impossible to state definitely the exact colour or the exact duration of the colour that will be obtained from varying quantities of methyl alcohol. In making this comparative test each solution must be added to the phloroglucin solution at the same time, so that the intensity and permanence of the colours may be judged by direct comparison.

Prescott Test (*Pharm. Archiv.*, 1901, iv., 86).—In this test the alcohol is oxidised by a heated copper spiral, hydrogen peroxide is added to destroy the acetaldehyde, the excess of hydrogen peroxide is removed by sodium thiosulphate, and the formaldehyde tested for by phloroglucin. This shows 5 per cent methyl alcohol in ethyl. It is difficult to get correct results with this test, because the action of the hydrogen peroxide and the thiosulphate seems to go wrong at times. The Haigh test is much more satisfactory.

Haigh Test (*Pharm. Reviews*, 1903, xxi., 404).—In this test the alcohol is oxidised by a heated copper spiral, the acetaldehyde removed by boiling the filtered solution till little or no odour is left, and the phloroglucin test used to show the presence of formaldehyde. The colour from methyl alcohol is said to last two to three minutes, that from ethyl alcohol to be faint and quickly to disappear. This shows 5 per cent methyl alcohol in ethyl. The time required, including the blank of ethyl alcohol, is about fifteen minutes.

The test is as satisfactory as any that uses phloroglucin. By adding alkali and heating the solution after it has been mixed with the phloroglucin (as previously described) it is possible to show 3 per cent to 4 per cent methyl alcohol by this test. The fact noted by Haigh that after one-half hour to one hour the solution from ethyl alcohol gives a blue colour, is due in my opinion to the phloroglucin alone (possibly the colour comes from some oxidation reaction), and has nothing to do with ethyl alcohol or its oxidation products.

Since acetaldehyde in small amounts gives no colour with alkaline phloroglucin, the question naturally arises, what is the reason for its removal in the Prescott and the Haigh tests? The answer is very simple—there is no need of removal. The working of the test has been misunderstood. When ethyl alcohol is oxidised, sufficient formaldehyde is produced to give a fairly deep and permanent colour with alkaline phloroglucin solution, which is quite a delicate reagent for the detection of formaldehyde. The

processes employed for the removal of acetaldehyde remove at the same time so much formaldehyde that the reaction with phloroglucin is reduced to a minimum. When methyl alcohol is present, sufficient formaldehyde is left to give a well-marked reaction. The experiments on the duration of colour, given under the general treatment of the phloroglucin reaction, show this very clearly.

Sangle-Ferrière-Cumiassé Test (*Ann. Chim. Anal. Appl.*, 1903, viii., 82).—This consists in oxidation of a cold dilute solution by potassium permanganate and sulphuric acid. The excess of permanganate is reduced by tannin, the solution is made faintly alkaline, and the manganese dioxide filtered off. The filtrate is tested by alkaline phloroglucin. It is said to show 1 per cent methyl alcohol in ethyl.

The test has a simple procedure, but the length of time necessary to oxidise the alcohol in order to get satisfactory results seems to vary with the room temperature, the amount of alcohol present, and the method of adding the sulphuric acid. The recommendation is made to confirm the test by acidifying and testing with gallic acid. This confirmation I regard as valueless, because of the great delicacy of the gallic acid test for formaldehyde. Ethyl alcohol often gives with phloroglucin quite a deep colour, not the faint colour mentioned in the description of the test.

Choice of Tests.

This will vary with circumstances. Unless there is supposed to be only a very small amount of methyl alcohol present, I should recommend trying first the simple Mulliken-Scudder test, which shows 8 per cent to 10 per cent and takes but a few minutes; next the Pharmacopœia test, which shows 2 per cent and takes fifteen minutes. If that gave no indication at all, the Trillat test should be used, but if there was any indication of the possible presence of methyl alcohol or a suspicion that it was there, I should advise rather than use the Trillat test to concentrate by distillation through a Hempel tube or Le Bel-Henninger tube or some such device, and then to use one of the shorter tests. This can be done much more quickly and easily than most persons suppose. In experiments to test the efficiency of the process when only small amounts of liquid are available, I used 25 c.c. of a mixture of 1 per cent methyl alcohol and 99 per cent ethyl alcohol. This was fractionated through a Hempel tube made of a glass tube 22.5 c.m. long, 1.7 c.m. in diameter, filled with glass beads about 3 m.m. in diameter. The beads held about 3½ c.c. of liquid that would not drain back into the flask. Three fractionations were made, taking the first time 15 c.c., then 7½ c.c., and finally 2 c.c. One c.c. of this last fraction was diluted, oxidised by a heated copper spiral, boiled down one-half over a free flame, and tested by resorcin. Moderately thick red flocks appeared. The total time consumed was one hour (this includes the time taken in allowing the liquid to drain back into the flask, a procedure necessary when such small quantities of liquid are being fractionated in this way). The Trillat test would have taken five hours. The Sangle-Ferrière-Cumiassé test is claimed to have a delicacy sufficient to show this amount of methyl alcohol, but I am doubtful about its indications. None of the other tests is sufficiently delicate to use in such a case.

The great value of the resorcin test is in the positive evidence given and the advantage of having some idea in a rough way of the quantity of formaldehyde present. The formation of flocks of characteristic colour shows positively the presence of a certain amount of formaldehyde, and no comparative test with ethyl alcohol is necessary. If there is only a contact ring and no flocks, there is very little formaldehyde present. When more is present there will be scanty small flocks. When much is present, the flocks are thick and abundant.

Mixtures.

In consequence of the great number of organic compounds, it is impossible to devise a test that will show a particular compound in any possible mixture. Certain general principles can be given, and by the aid of these and by a

clear understanding of what the test used will show and what are its possibilities of error, the detection of methyl alcohol ought to be certain except when it is present in very small quantities, and there is not sufficient material to allow of concentration.

If formaldehyde is present, it must be removed, if any of the oxidation tests are used, since they are all dependent on conversion of the alcohol to formaldehyde or methylal. This may be accomplished by digestion with ammonia; by digestion cold with excess of sodium bisulphite for four to five hours (Bamberger, *Zeit. Angew. Chem.*, 1904, xvii., 1246); by digestion at 70–80° in a stoppered bottle with resorcin and sulphuric acid for two to three hours (Mulliken, Scudder, *Am. Chem. Journ.*, 1900, xxiv., 449); or by boiling with a return condenser with aniline and phosphoric acid (Allen, Chataway, *Analyst*, 1891, xvi., 113). The liquid is then distilled, the formaldehyde remaining behind in combination. The distillate should always be tested for aldehyde to make sure that the removal is complete. Other means that may prove useful in certain cases are digestion hot with sodium sulphite (Lemme, *Chem. Zeitung*, 1903, xxvii., 896), or with hydrazine sulphate (Pfaff, *Chem. Zeitung*, 1902, xxvi., 701). When difficulty is found in removing all the formaldehyde, it is often possible without further treatment to make a rapid test which either will show the presence of methyl alcohol or will make further investigation desirable. Under these conditions little formaldehyde will be present, and the resorcin test used before oxidation will show only a contact ring. When the solution is oxidised and the resorcin test again applied, if methyl alcohol is present, the increased amount of formaldehyde will be shown either by the presence of flocks or by thickening of the ring. The presence of flocks in such a case would be almost conclusive evidence of the presence of methyl alcohol. Fractional distillation is often of great help in such cases. Gnehm and Käufer (*Zeit. Angew. Chem.*, 1905, xviii., 93) state that in the estimation of methyl alcohol in formaldehyde, when the formaldehyde is condensed with sodium sulphanilate, and the alcohol distilled off, the distillate always contains small quantities of compounds having the characteristic odour of formaldehyde and the power of reducing silver nitrate, but that these compounds are unsaturated bodies of unknown nature.

Other aldehydes can be removed by digestion with resorcin and sulphuric acid, or with aniline and phosphoric acid. Their presence is indicated by the usual aldehyde reactions or by the resorcin test.

Phenols and bases will combine with any formaldehyde that may be made in the course of a test. They must therefore be removed—by distillation from sodium or potassium hydroxide in the case of phenols (this treatment also removes acids)—by distillation from dilute sulphuric acid in the case of bases.

Various compounds such as colouring-matters, &c., can be removed by simple or fractional distillation, by filtration through bone-black with or without previous treatment by lime, or by extracting the alcohol with water and testing the aqueous extract after distillation.

It is best to test only solutions wholly soluble in two to three parts of water, that will distil between 50° and 100°.

Thermo-chemistry of Hydrazones.—Ph. Landrieu.—The author finds that the heat evolved during the action of the acetones and aldehydes on phenylhydrazine is practically constant; it varies between 12 cal. and 16 cal. This number is slightly higher than that obtained during the reaction of the aldehydes or acetones on hydroxylamine with formation of oximes, the latter having the value 10 cal. to 13 cal. This explains the displacement of hydroxylamine by phenylhydrazine and the formation of hydrazone.—*Comptes Rendus*, cxli., No. 6.

* Mulliken, Scudder (*Amer. Chem. Journ.*, xxiv., 447). The question is here treated entirely from the standpoint of the resorcin test, but the general principles remain the same.

THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND. SCHEME FOR EXAMINATIONS IN TECHNICAL CHEMISTRY.

THE Scheme for Examinations in Technical Chemistry which the Council of the Institute has decided to adopt should tend to promote the efficiency of chemists in works, though it is obvious that the qualifications to pass such examinations can only be obtained by actual practice in the works themselves.

Examinations are, at the best, a clumsy way of sorting the capable from the incapable men, and we are not inclined to think that a written examination is the best means for picking out the men best qualified in purely practical work. However, until some better method is devised we must needs fall back on the barbarous means at present in use.

The following is the gist of the scheme about to be adopted by the Council of the Institute of Chemistry:—

1. The Council has resolved to hold examinations in the industrial applications of chemistry and to grant certificates in respect thereof.
2. These examinations will be open only to Fellows, and to those Associates who have been registered as such for at least one year.
3. Candidates will be required to produce evidence of practical technical training.
4. The examinations will comprise the following:—
 - a. The application of well-known chemical and physical laws to industrial operations.
 - b. The development, control, and transmission of power and heat.
 - c. A working knowledge of operations and plant of which general use is made in industrial works for the treatment and handling of materials, finished products, waste products, and effluents, including a practical acquaintance with fittings and stores.
 - d. The properties of materials affecting their application to the construction of plant and apparatus in chemical works.
 - e. Some ability in interpreting drawings of chemical plant and in making dimensioned rough sketches.
 - f. The calculation of working costs, and a general knowledge of the clerical work connected with manufacturing operations.
5. Each candidate will be required to select one important industry in which his knowledge of the above subjects may be tested. Questions which might involve the disclosure of unpublished processes and details of plant in particular works will not be asked. All candidates will be expected to give evidence of a general knowledge of chemical technology. The Examiners will take into account original work and special knowledge, but not so as to excuse the candidate from any part of the examination.

In making this scheme the basis for examinations in technical chemistry, the Council wishes generally to indicate the knowledge a candidate should possess. The Fellow or Associate, who by his previous examinations and work has proved that he possesses the theoretical knowledge necessary for his profession, and is efficient in practical laboratory work, should at this examination show that he has learnt the industrial application of his science, and has by practical experience acquired the habit of thinking and working industrially. He should show a practical knowledge of operations, both chemical and mechanical, and of the apparatus and machinery commonly used in chemical manufactures. He should be a chemist, with so much knowledge of chemical technology and engineering, that he can intelligently and economically supervise manufacturing operations, and that, when suggesting improvements or new manufactures, he can advise as to the apparatus and machinery required. He should be able "to think in tons," and know how profits are made.

Fellows and Associates desiring to take the examination

will be required to produce evidence of practical technical training distinct from the course for the Associateship. Experience of not less than one year in practical manufacture, or an equivalent amount of training, would constitute evidence satisfactory to the Council, who will be prepared, at first, to interpret Clause 3 very broadly.

The Council desires to encourage young chemists to take post-graduate training and to gain practical experience; also, to urge universities and technical colleges to establish special courses, under teachers of experience and in suitably equipped workshops, for instruction in chemical technology. Steps in this direction are being taken in various parts of the country, and in some instances provision is being made for teaching the methods of applied chemistry on a fairly large scale.

The form of the examinations, the exact dates when the first examination shall be held, the time it shall occupy, the fee, and other details will be published in due course.

NOTICES OF BOOKS

The Crystallisation of Iron and Steel. By J. W. MELLOR, D.Sc. London, New York, and Bombay: Longmans, Green, and Co. 1905.

THIS book contains a course of six lectures delivered to the engineering students of the Staffordshire County Technical Classes at the Newcastle High School in November and December, 1904, and gives a summary of the most important results which have been obtained recently with regard to alloys of iron and steel. The first lecture discusses the solidification and cooling of alloys, and from it the student should be able to acquire very readily clear and accurate ideas concerning transition temperatures, cooling curves, &c. The second lecture deals with the constituents of iron and steel and the phase rule, the numerical examples which are interspersed being of great value in establishing the student's knowledge, and showing him how to apply it practically. The hardening, annealing, and tempering of steel and the influence of stress and strain are treated in the most graphic manner in subsequent lectures, which are all well illustrated, and contain copious references for those who wish to pursue the subject further. The last lecture deals with the preparation of a specimen for the microscope, and gives a rough estimate of the time required to obtain a micro-photograph of the structure of a metal, and also of the outfit required for this purpose and its approximate cost. An appendix contains a glossary of terms, and in many cases gives their French and German equivalents, and is not the least useful feature of a thoroughly practical book, which illustrates the author's power of inspiring interest and instilling a knowledge of facts simultaneously.

Higher Mathematics for Students of Chemistry and Physics. By J. W. MELLOR, D.Sc. Second Edition. London, New York, and Bombay: Longmans, Green, and Co. 1905.

THE new edition of this most useful book has been re-written, and while the general plan is unaltered some changes have been made in the details of the arrangement, and fuller explanations are given of points which appear to present special difficulties. Some new sections are added, e.g., on the theory of the washing of precipitates, the tests for the convergency of series, and the calculus of variations. All the alterations which have been made serve to increase the value of the book, which has been much appreciated both by students and teachers.

The Theory of Experimental Electricity. By WILLIAM CECIL DAMPIER WHETHAM, M.A., F.R.S. Cambridge: University Press. 1905.

THE study of this work cannot fail to develop in the student an interest in the problems of electricity, for the

author has recognised the great value of giving his readers an insight into research, so that they may realise that the science is still in a state of growth. Thus he does not hesitate to touch upon debatable points and to dwell shortly upon hypotheses which very likely will not stand the test of future developments; he alludes to work which is now being done, and does so in such a way as to stimulate the desire for more knowledge, and to show the student how to acquire it most easily and satisfactorily. The book hardly takes the place of an ordinary text-book of electricity, and, indeed, was written more especially as a supplement and book of reference for the author's own students who were attending a course of lectures upon the elementary theory of electricity. It is not a cram book suitable for the use of examination candidates, but is rather a scholarly exposition of the subject, having a considerable literary value. Certain branches which have seen special development recently, such as electrolysis, conduction through gases, and radio-activity, are treated rather more fully than in the usual text-books, and the chapters on these subjects contain the essentials most lucidly and interestingly treated.

Outlines of Physiological Chemistry. By S. P. BEEBE, Ph.D., and B. H. BUXTON, M.D. New York: The Macmillan Company. London: Macmillan and Co., Ltd. 1904.

THIS book attacks the subject of physiological chemistry only from the theoretical side, and deals almost exclusively with the chemistry of certain compounds which are of physiological interest. A knowledge of inorganic chemistry is assumed, but the theory of solutions is briefly discussed, and nearly half the book is devoted to the consideration of elementary organic chemistry, illustrated chiefly by substances which are of importance in physiology. The remainder of the book deals with the composition and properties of the proteids and the enzymes. The chemistry of the secretions of the animal body, of the tissues, and of respiration are subjects which are omitted, although room is found for a chapter on disease and immunity. Thus it will be seen that the book forms rather a preparation for the study of physiological chemistry, and even from this point of view it is hardly satisfactory, for the student would be able to find practically all that is in the first part of the book in a text-book of organic chemistry, and, moreover, would require a more extended knowledge of the subject before attacking physiological chemistry. The work suffers throughout from a want of cohesion and system, and is exceedingly sketchy in places, suggesting notes jotted down more or less at random.

A Primer of Explosives. By Major A. COOPER-KEY. Edited by Captain J. H. THOMSON. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1905.

THIS little book is intended for the use of local inspectors and dealers, and is not a scientific treatise on explosives. It is consequently written in untechnical language, and really constitutes a brief commentary on the Explosives Act. A description is given of the nature of an explosive, and the composition and use of each class of explosive, as classified in the Order in Council made under Section 106 of the Act, are discussed, special stress being laid upon the dangers attending the use of each class. The last chapter contains suggestions on the storing of explosives, precautions to be observed, and the safest methods for destroying gunpowder and all blasting materials.

A Treatise on Chemistry. By Sir H. E. ROSCOE, F.R.S., and C. SCHORLEMMER, F.R.S. Volume I. *The Non-metallic Elements.* Third Edition. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1905.

IN preparing for the press the third edition of this treatise Sir Henry Roscoe, assisted by Drs. H. G. Colman and A.

Harden, has carefully revised the text in order to bring it thoroughly up to date. Every effort in the way of consulting the most recent authoritative literature appears to have been made to render the work as complete and trustworthy as possible, and, as in the earlier editions, special attention has been paid to the description of such technical processes as the manufacture of sulphuric acid and of coal-gas. The pages on the atmosphere may be specially mentioned as forming an excellent example of how a subject may be presented with perfect scientific accuracy and considerable attention to detail, and yet in such a manner as to excite interest to the fullest degree.

Sugar and the Sugar-cane. By NOEL DEERR. Altrincham (Manchester): Norman Rodger. 1905.

This work aims at covering a large field, for in it is given a complete account of the sugar industry, from the agriculture of the cane to the analysis of sugar-house products. The treatment of such a range of subjects within a limited space necessitates the sacrifice to a certain extent of some branches, and in this case it is chiefly the scientific aspect which has suffered, although it is not by any means altogether neglected. The author has studied the standard works on the sugar-cane, and, moreover, gives his readers the benefit of the conclusions to which he himself has come, as regards many practical details, after years of experience. These personal opinions are in themselves of no mean value. Besides discussing the cultivation of the cane and the extraction and treatment of the juice, the author enters at some length upon the question of the control of the factory, considering it more especially from the point of view of those factories in which a chemist is not employed, and in which the apparatus and fittings are reduced to the minimum absolutely necessary for sugar analysis only.

Methods of Chemical Control in Cane-sugar Factories. By H. C. PRINSEN GEERLIGS. Altrincham (Manchester): Norman Rodger. 1905.

THE greater part of the matter in this book has already been published in the *International Sugar Journal*, 1904, vol. vi., and now appears in book-form with the addition of many tables which are constantly required for reference in the sugar laboratory. The work contains directions for the laboratory work, and calculations necessary to enable the chemist to draw up the usual detailed daily, and fortnightly or monthly reports; also a list of the instruments and utensils required, together with explicit instructions for verifying the measuring tanks and vessels, and it will form a valuable addition to the library of the chemist employed in sugar-works.

Leather for Libraries. By E. WYNDHAM HULME, J. GORDON PARKER, A. SEYMOUR-JONES, CYRIL DAVENPORT, and F. J. WILLIAMSON. London: The Library Supply Co. 1905.

THIS small book, published for the Sound Leather Committee of the Library Association, gives many useful hints for the benefit of librarians and others, and though some of its recommendations may be regarded somewhat in the light of counsels of perfection, undoubtedly many malpractices have crept into the process of preparing leather for the binder, and warnings on these points are well worth noting by those who are interested in book-binding. The question that rises naturally in the mind of the reader is whether it is much good to make efforts to ensure the durability of the outer coverings of books when the paper of which they are made has shown such marked deterioration lately. Be this as it may, the book will no doubt be read with interest; it contains thoroughly practical directions for the binding and repairing of books for public libraries, and chapters on the history of tanning, the causes of the decay of leathers, and the characteristics and values of modern book-binding leathers, six specimens of which are attached to the covers.

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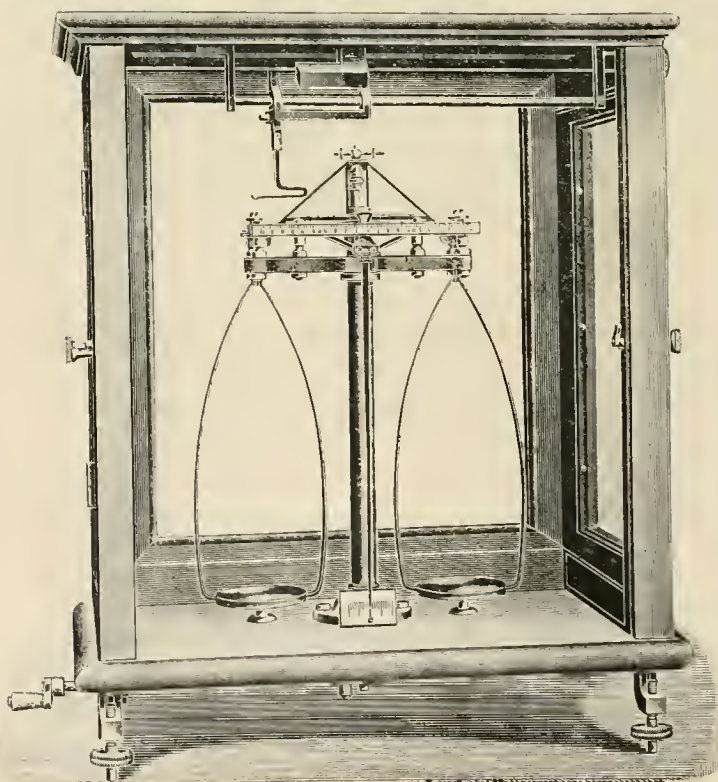
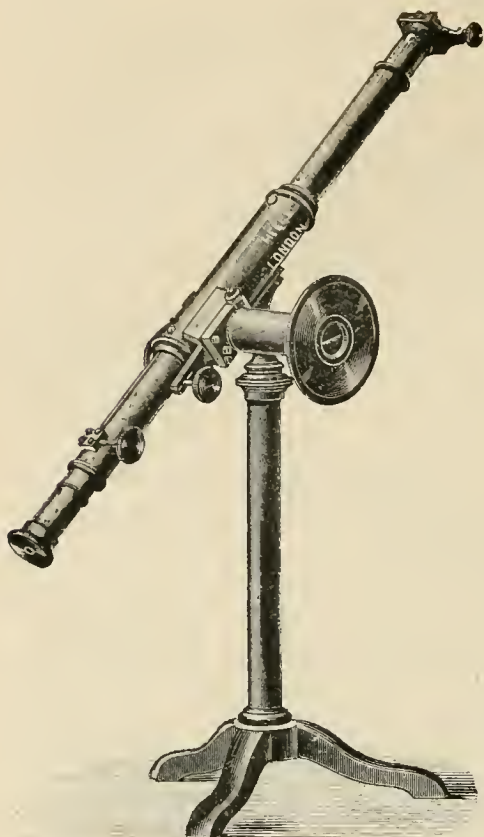
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DIAMONDS.

A LECTURE DELIVERED BEFORE THE BRITISH ASSOCIATION
AT KIMBERLEY, SEPTEMBER 5, 1905.

By Sir WILLIAM CROOKES,
Hon. D.Sc. (Oxford and Dublin), F.R.S.

(Concluded from p. 150).

Physics of the Diamond.

I WILL now briefly survey the chief chemical and physical characteristics of the diamond, showing you by the way a few experiments that bear upon the subject.

The black inclusions in some transparent diamonds consist of graphite. On crushing a clear diamond showing such spots and heating in oxygen to a temperature well below the point at which diamond begins to burn, Moissan found that the grey tint of the powder disappeared, no black spots being seen under the microscope. There also occur what may be considered intermediate forms between the well-known crystallised diamond and graphite. These are "boart" and "carbonado." Boart is an imperfectly crystallised diamond, having no clear portions, and therefore useless for gems. Boart is frequently found in spherical globules, and may be of all colours. It is so hard that it is used in rock-drilling, and when crushed it is employed for cutting and polishing other stones. Carbonado is the Brazilian term for a still less perfectly crystallised form of carbon. It is equally hard, and occurs in porous masses, and in massive black pebbles, sometimes weighing a couple or more ounces.

Crystallisation.

The diamond belongs to the isometric system of crystallography; the prevailing form is octahedral. It frequently occurs with curved faces and edges. Twin crystals (macles) are not uncommon.

On the table I have models of various crystalline forms of native diamonds.

No. 20. Diamond in the form of a hexakisoctahedron (the forty-eight scalenohedron), or a solid figure contained by forty-eight scalene triangles. According to Professor Maskelyne, this occurs as a self-existent form only in the diamond.

No. 59. Diamond in the form of a hexakisoctahedron and octahedron. From Sudafrika.

No. 105. Diamond in the form of octahedron with inter-sections.

No. 127. Diamond from Brazil.

No. 128. Diamond from Sudafrika.

No. 129. Diamond from Brazil.

A macle or twin crystal, showing its formation from an octahedron with curved edges.

The use of diamond in glass cutting I need not dwell on. So hard is diamond in comparison to glass, that a suitable splinter of diamond will plane curls off a glass plate as a carpenter's tool will plane shavings off a deal board. On the screen I show a few diamond-cut glass shavings.

Many crystals of diamonds have their surfaces beautifully marked with equilateral triangles, interlaced and of varying sizes. Under the microscope these markings appear as shallow depressions sharply cut out of the surrounding surface; these depressions were supposed by Gustav Rose to indicate the probability that the diamonds at some previous time had been exposed to incipient combustion. Rose also noted that striations appeared on the surfaces of diamonds burnt before the blowpipe.

I have tried many times to imitate these markings by partial combustion of clear crystals of diamond, but have not succeeded in reproducing triangles of such beauty as you

see formed by nature. According to the crystalline face exposed to incipient combustion the etchings are triangular or cubical, and sometimes intermediate between the two. I throw on the screen magnified photographs of these etchings, and you will observe that while the triangular or box like tendency is very apparent, there is an absence of regularity and sharpness.

The artificial markings are closer massed, looking as if the diamond during combustion had been dissected into triangular and rectangular flakes, while the markings natural to crystals appear as if produced by the crystallising force as they were being built up.

Certain artificial diamonds present the appearance of an elongated drop. I have seen diamonds which have exactly the appearance of drops of liquid separated in a pasty condition and crystallised on cooling. Diamonds are sometimes found with little appearance of crystallisation, but with rounded forms similar to those which a liquid might assume if kept in the midst of another liquid with which it would not mix. Other drops of liquid carbon retained for sufficient time above their melting-point would coalesce with adjacent drops, and on slow cooling would separate in the form of large perfect crystals. Two drops, joining after incipient crystallisation, might assume the not uncommon form of interpenetrating twin crystals. Illustrations of all these caprices are here to-night.

Again, diamond crystals are generally perfect on all sides. They show no irregular side or face by which they were attached to a support, as do artificial crystals of chemical salts; another proof that the diamond must have crystallised from a dense liquid.

Having no double refraction the diamond should not act on polarised light. But as is well known, if a transparent body which does not so act is submitted to strain of an irregular character it becomes doubly refracting, and in the polariscope reveals the existence of the strain by brilliant colours arranged in a more or less defined pattern according to the state of tension in which the crystal exists. I have examined many hundred diamond crystals under polarised light, and with few exceptions all show the presence of internal tension. I will project some diamonds on the screen by means of the polarising microscope, and you will see by the colours how great is the strain to which some of them are exposed. On rotating the polariser, the black cross most frequently seen revolves round a particular point in the inside of the crystal; on examining this point with a high power, we sometimes see a slight flaw, more rarely a minute cavity. The cavity is filled with gas at enormous pressure, and the strain is set up in the stone by the effort of the gas to escape. I have already told you that the great Cullinan diamond by this means reveals a state of internal stress and strain.

It is not uncommon for a diamond to explode soon after it reaches the surface; some have been known to burst in the pockets of the miners or when held in the warm hand, and the loss is the greater because large stones are more liable to explode or fly in pieces than small ones. Valuable stones have been destroyed in this way, and it is whispered that cunning dealers are not averse to allowing responsible clients to handle or carry in their warm pockets large crystals fresh from the mine. By way of safeguard against explosion, some dealers imbed large diamonds in raw potato to insure safe transit to England.

The anomalous action which many diamonds exert on polarised light is not such as can be induced by heat, but it can easily be conferred on diamonds by pressure, showing that the strain has not been produced by sudden cooling but by sudden lowering of pressure.

The illustration of this peculiarity is not only difficult, but sometimes exceedingly costly—difficult because it is necessary to arrange for projecting on the screen the image of a diamond crystal between the jaws of a hydraulic press, the illuminating light having to pass through delicate optical polarising apparatus—and costly because only perfect, clear crystals can be used, and crystals of this character sometimes fly to pieces as the pressure rises. No colour as yet

is seen on the screen, the crystal not being birefringent. A movement of the handle of the press, however, gives the crystal a pinch, instantly responded to by the colours on the screen, showing the production of double refraction. Another movement of the handle brightens the colours; a third may strain the crystal beyond its power of resistance, so I refrain.

Hardness.

Diamonds vary considerably in hardness, and even different parts of the same crystal differ in their resistance to cutting and grinding.

Beautifully white diamonds have been found at Inverel, New South Wales, and from the rich yield of the mine and the white colour of the stones, great things were expected. In the first parcel which came to England the stones were found to be so much harder than South African diamonds that it was at first feared they would be useless except for rock boring purposes. The difficulty of cutting them disappeared with improved appliances, and they now are highly prized.

The famous Koh-i-noor, when cut into its present form, showed a notable variation in hardness. In cutting one of the facets near a yellow flaw, the crystal became harder and harder the further it was cut, and after working the mill for six hours at the usual speed of 2400 revolutions a minute, little impression was made. The speed was increased to more than 3000, when the work slowly proceeded. Other portions of the stone were found to be comparatively soft, and hardened as the outside was cut away.

I can illustrate the intense hardness of the diamond by experiment. On the flattened apex of a conical block of steel I place a diamond, and upon it I bring down a second cone of steel. With the lamp I project an image of the diamond and steel faces on the screen, and force them together by hydraulic power. I can squeeze the stone into the steel blocks without injuring it in the slightest degree.

The pressure gauge shows (60) atmospheres, and the piston being 3.2 inches diameter, the absolute pressure is (3.16) tons, equivalent on a diamond of (12) square m.m. surface to (170) tons per square inch of diamond.

Although not directly bearing on the subject I will introduce the only serious rival of the diamond as regards hardness. It is the metal tantalum, a fine specimen of which I owe to Messrs. Siemens Brothers. A hole had to be bored through a plate of this metal, and a diamond drill was used revolving at the rate of 5000 revolutions per minute. This whirling force was continued ceaselessly for three days and nights, when it was found that only a small depression $\frac{1}{2}$ m.m. deep had been drilled, and it was a moot point which had suffered most damage, the diamond or the tantalum (W. von Bolton, *Zeitschr. Elektrochem.*, ii., 45—51, Jan. 20, 1905). In another respect tantalum is likely to rival graphitic carbon, as it has rivalled adamantite carbon. Its thin wire is extensively used for filaments of incandescent electric lamps; it shows a much higher efficiency than does the old carbon filament. The melting-point of tantalum is about 2300° C., a temperature seldom or never reached in an ordinary lamp.

Density.

The following table gives the specific gravities of the minerals found on the sorting tables:—

	Specific gravity.
Hard graphite	2.5
Quartzite and granite	2.6
Beryl	2.7
Mica	2.8
Hornblende	3.0
Boart	3.47—3.49
Carbonado	3.50
Diamond	3.514—3.518
Garnet	3.7
Corundum	3.9
Zircon	4.4
Barytes	4.5
Chrome and titanitic iron ore ..	4.7
Magnetite	5.0

I have here a liquid, the double nitrate of silver and thallium, which while solid at ordinary temperatures, liquefies at 75° C., and then has a specific gravity of 4.5. Admixture with water lowers the density to any desired point.

In the projection apparatus I have a glass cell containing this liquid diluted to a density of about 3.6. I throw in pieces of the above named minerals, and you see all those whose density is lower than 3.6 rise to the surface, while the denser minerals sink. I now carefully add a little water and stir well, until I have reduced the density of the liquid to that of the diamond, when the heterogeneous collection sorts itself into three parts. The graphite, quartz, beryl, mica, and hornblende rise to the surface; the garnet, corundum, zircons, &c., sink to the bottom, while the diamonds float in the middle of the liquid. With a platinum landing net I skim off the swimmers and put them into one dish; with the same net I fish out the diamonds and put them in a second dish, while by raising a sieve at the bottom I remove the heavy minerals and put them into a third. The accurate separation of diamonds from the heterogeneous mixture has been effected in less time than has taken me to describe the experiment.

The table shows that diamonds vary somewhat in density among themselves, between narrow limits. Here is an illustration. I have a flat test-tube in which I have some of the same dense liquid, and in it are three selected diamonds. One rises to the top, another floats uncertain where to settle, rising and falling as I raise or lower the temperature of the sorting liquid, whilst the third sinks to the bottom. Allowing the liquid to cool a degree or two slightly increases the density and sends all three to the surface.

Refractivity.

But it is not the hardness of the diamond so much as its optical qualities that make it so highly prized. It is one of the most refracting substances in nature, and it also has the highest reflecting properties. In the cutting of diamonds advantage is taken of these qualities. When cut as a brilliant the facets on the lower side are inclined so that light falls on them at an angle of 24° 13', at which angle all the incident light is totally reflected. A well cut brilliant should appear opaque by transmitted light except at a small spot in the middle where the table and culet are opposite. All the light falling on the front of the stone is reflected from the facets, and the light passing into the diamond is reflected from the interior surfaces and refracted into colours when it passes out into the air, giving rise to the lightnings, the effulgence, and coronations for which the diamond is supreme above all other gems.

I hold some cut diamonds in the electric light; by transmitted light you see they are black, while by reflected light they fill the room with radiance, dazzle, and colour.

The following table gives the refractive indices of diamonds and other bodies:—

Refractive Indices for the D Line.

Chromate of lead	2.50—2.97
Diamond	2.47—2.75
Phosphorus	2.22
Sulphur	2.12
Ruby	1.78
Thallium glass	1.75
Iceland spar	1.65
Topaz	1.61
Beryl	1.60
Emerald	1.59
Flint glass	1.58
Quartz	1.55
Canada balsam	1.53
Crown glass	1.53
Fluor-spar	1.44
Ice	1.31

In vain I have searched for a liquid of the same refraction as diamond. Such a liquid would be invaluable to the

merchant, as on immersing a stone the clear body would absolutely disappear, leaving in all their ugliness the flaws and black specks so frequently seen even in the best stones.

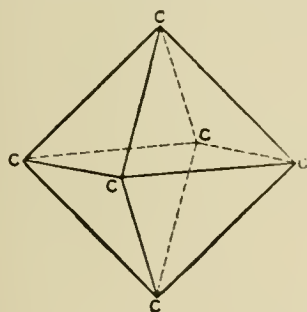
Arguing from theoretical considerations connected with the Specific Refractive Energy of diamond, and employing Lorentz's expression for refraction—

$$\left(\frac{\mu^2 - 1}{\mu^2 + 2}\right) \frac{P}{d},$$

in which μ = refractive index;
 $\mu^2 - 1$ = refractive energy;
 d = density;
 P = molecular weight.

Brühl has shown that diamond is perfectly normal in its optical properties, and has an atomic refraction = 5. He has put forward the speculation that the diamond may be the last member of the paraffin series of which marsh-gas is the first.

"Now we can imagine," says Brühl (*Proceedings of the Royal Institution*, May 26, 1905), "why the diamond, i.e., pure crystallised carbon, is optically normal. We obtain an idea of the mineral's chemical constitution, and of the way in which the atoms of carbon are perhaps combined in the sparkling gem. The diamond cannot possibly contain any double bonds. Imagine, however, at each of the six corners of a regular octahedron, a single molecule of marsh-gas, CH_4 , i.e., altogether C_6H_{24} , and then imagine all the 24 hydrogen atoms successively removed, so that each carbon atom is connected with each of its neighbours only by a single bond, and thus all six atoms of carbon are united together in a single whole. Then you obtain, as the most simple representation of the molecule of the diamond, a regular octahedron, with one atom of carbon at each of its six corners, whilst the edges represent the mutual bonds:—



Several simple molecules of this kind may be combined into one crystallised particle of the spectrochemically normal diamond."

Absorption Spectrum of Diamond.

On passing a ray of light through a diamond and examining it in a spectroscope, B. Walter has found in all colourless brilliants of over one carat in weight, an absorption band at wave-length 4155 (violet). He ascribes this band to an impurity and suggests it may possibly be due to samarium. Three other fainter lines were detected in the ultra-violet by means of photography.

Phosphorescence of Diamond.

After exposure for some time to the sun many diamonds glow in a dark room. Some diamonds are fluorescent, appearing milky in sunlight. In a vacuum, exposed to a high-tension current of electricity, diamonds phosphoresce of different colours, most South African diamonds shining with a bluish light. Diamonds from other localities emit bright blue, apricot, pale blue, red, yellowish green, orange, and pale green light. The most phosphorescent diamonds are those which are fluorescent in the sun. One beautiful green diamond in my collection, when phosphorescing in a

good vacuum, gives almost as much light as a candle, and you can easily read by its rays. But the time has hardly come when diamonds can be used as domestic illuminants! The emitted light is pale green, tending to white, and in its spectrum, when strong, can be seen bright lines, one at about λ 5370 in the green, one at λ 5130 in the greenish blue, and one at λ 5030 in the blue.

After many years' bombardment in a vacuum tube this diamond grew very dark, almost black on the surface. Heating in a mixture of nitric acid and potassium chlorate scarcely changed the colour. The action of heat was then tried, and on slowly heating to about 500° C. the dark colour entirely disappeared, and the original milky green appearance was restored. Although I watched narrowly I could see no trace of phosphorescence during the heating.

Diamonds which phosphoresce red generally show the yellow sodium line superposing on a continuous spectrum. In one Brazilian diamond phosphorescing a reddish yellow colour, I detected the citron line characteristic of yttrium.

By permission of Mrs. Kunz, wife of the well known New York mineralogist, I will show you perhaps the most remarkable of all phosphorescing diamonds. This prodigy diamond will phosphoresce in the dark for some minutes after being exposed to a small pocket electric light, and if rubbed on a piece of cloth a long streak of phosphorescence appears.

The rays which make the diamond phosphoresce are high in the ultra-violet. A thin sheet of glass cuts them all off. To illustrate this phosphorescence under the influence of the ultra-violet rays, I have arranged a powerful source of these rays, and in front I expose a design made up of certain minerals—willemite, franklinite, calcite, &c.,—phosphorescing of different colours. Their brilliant glow ceases entirely when I interpose a thin piece of glass between them and the ultra-violet lamp.

Tribo-luminescence.

A few minerals give out light when rubbed, and Mrs. Kunz's diamond is equally striking in this respect. In the year 1663 the Hon. Robert Boyle read a paper before the Royal Society, in which he described several experiments made with a diamond which markedly showed tribo-luminescence. As specimens of tribo-luminescent bodies I show you sphalerite (sulphide of zinc) and an artificial sphalerite, which is even more responsive to friction than the native sulphide.*

Combustion of the Diamond.

When heated in air or oxygen to a temperature varying from 760° to 875° C. according to its hardness, the diamond burns with production of carbonic acid. It leaves an extremely light ash, sometimes retaining the shape of the crystal, consisting of iron, lime, magnesia, silica, and titanium. In boart and carbonado the amount of ash sometimes rises to 4 per cent, but in clear crystallised diamonds it is seldom higher than 0.05 per cent. By far the largest constituent of the ash is iron.

The following table shows the temperatures of combustion in oxygen of different kinds of carbon:—

	°C.
Condensed vapour of carbon	650
Carbon from sugar, heated in an electrical furnace	660
Artificial graphites, generally	660
Graphite from ordinary cast-iron	670
Carbon from blue ground, of an ochrey colour	690
" " " " very hard and black	710
" " " " soft Brazilian	760
" " " " hard Kimberley	780
Boart from Brazil	790
" " " " from Kimberley	790
" " " " very hard, impossible to cut	900

* Artificial tribo-luminescent sphalerite:—

Zinc carbonate	100 parts
Flower of sulphur	30 "
Manganese sulphate	$\frac{1}{2}$ per cent

Mix with distilled water and dry at a gentle heat. Put in luted crucible and keep at a bright red heat for from two to three hours.

Action of Radium on Diamond.

The β -rays from radium having like properties to the stream of negative electrons in a radiant matter tube, it was of interest to ascertain if they would exert a like difference on diamond. The diamond glows under the influence of the β -radiations, and crushed diamond cemented to a piece of card or metal makes an excellent screen in a spintharoscope—almost as good as zinc sulphide. Some fine colourless crystals of diamond were embedded in radium bromide and kept undisturbed for more than twelve months. At the end of that time they were examined. The radium had caused them to assume a beautiful blue colour, and their value as “fancy stones” had been materially increased. Here are a couple of diamonds originally of the same purity of water. One has been coloured by radium, the other is in its natural state. The colour of the radium tinted stone is very pronounced. The lantern slide shows the darkening thus produced. A and B are diamonds after twelve months burial in radium bromide; diamond C is of the original colour.

This blue colour is persistent and penetrates below the surface. It is unaffected by long continued heating in strong nitric acid and potassium chlorate, and is not discharged by heating to redness.

To find out if this prolonged contact with radium had communicated to the diamond any radio-active properties, six diamonds were put on a photographic plate, and kept in the dark for a few hours. I will project the image of the result after development. The three on the upper row are the diamonds which have had a prolonged sojourn with radium, the three below are similar diamonds picked out for comparison, which have not been near radium. See how strangely the three upper ones have acted. Notice also that by mere contiguity to the others the lower diamonds also shine with an induced, factitious radio-activity. I throw on the screen a magnified image of one of the blue crystals, and you see in how regular and geometrical a pattern the radio-active emanations radiate from the crystal. This observation has only been made a short time, and is still under investigation. Like the blue tint the radio-activity persists after drastic treatment. To me this proves that radio-activity does not merely consist in the adhesion of electrons or emanations given off by radium, to the surface of an adjacent body, but the property is one involving layers below the surface, and like the alteration of tint is probably closely connected with the intense molecular excitement the stone had experienced during its twelve months' burial in radium bromide.

A diamond that had been coloured blue by radium, and had acquired strong radio-active properties, was slowly heated to dull redness in a dark room. Just before visibility a faint phosphorescence spread over the stone. On cooling and examining the diamond it was found that neither the colour nor the radio-activity had suffered appreciably.

The diamond is remarkable in another respect. It is extremely transparent to the Röntgen rays, whereas highly refracting glass, used in imitation diamonds, is almost perfectly opaque to the rays. I exposed for a few seconds over a photographic plate to the X rays the large Delhi diamond of a rose-pink colour weighing 31½ carats, a black diamond weighing 23 carats, and a glass imitation of the pink diamond. On development, the impression where the diamond obscured the rays was found to be strong, showing that most rays passed through, while the glass was practically opaque. By this means imitation diamonds can readily be distinguished from true gems.

I have already signified that there are various degrees of refractoriness to chemical reagents among the different forms of graphite. Some dissolve in strong nitric acid; other forms of graphite require a mixture of highly concentrated nitric acid and potassium chlorate to attack them, and even with this intensely powerful agent some graphites resist longer than others. M. Moissan has shown that the power of resistance to nitric acid and potassium chlorate is in proportion to the temperature at which the graphite was formed, and with tolerable certainty we can estimate this

temperature by the resistance of the specimen of graphite to this reagent.

The superficial dark coating on a diamond after exposure to molecular bombardment I have proved to be graphite (CHEMICAL NEWS, vol. lxxiv., p. 39, July, 1896). M. Moissan has shown that this graphite, on account of its great resistance to oxidising reagents, cannot have been formed at a lower temperature than 3600° C. (*Comptes Rendus*, cxxiv., p. 653).

It is thus manifest that the bombarding electrons endowed with an electric charge, and striking the diamond with enormous velocity, raise the superficial layer to the temperature of the electric arc, and turn it into graphite, whilst the mass of diamond and its conductivity to heat are sufficient to keep down the general temperature to such a point that the tube appears scarcely more than warm to the touch.

A similar action occurs with silver, the superficial layers of which can be raised to a red heat without the whole mass becoming more than warm (*Proc. Roy. Soc.*, vol. l., p. 99, June, 1891).

I will now draw your attention to a strange property of the diamond, which at first sight might seem to discount the great permanence and unalterability of this stone. It has been ascertained that the cause of phosphorescence is in some way connected with the hammering of the electrons, violently driven from the negative pole, on to the surface of the body under examination, and so great is the energy of the bombardment, that impinging on a piece of platinum or even iridium, the metal will actually melt. When the diamond is thus bombarded in a radiant matter tube the result is startling. It not only phosphoresces, but assumes a brown colour, and when the action is long continued becomes almost black.

I will project a diamond on the screen and bombard it with radiant matter before your eyes. I do not like to anticipate a failure, but I am at the mercy of my diamond. I cannot rehearse this experiment, and it may happen that the diamond I have selected will show caprice and not blacken in reasonable time. Some diamonds visibly darken in a few minutes, while others, more leisurely in their ways, require an hour.

This blackening is only superficial, but no ordinary means of cleaning will remove the discolouration. Ordinary oxidising reagents have little or no effect in restoring the colour. The black stain on the diamond is due to a form of graphite which is resistant to oxidation.

Conversion of Diamond into Graphite.

Although we cannot convert graphite into diamond, we can change the diamond into graphite. I take a clear crystal of diamond and place it between two carbon poles, and throw the image on the screen by means of a powerful arc lamp behind. I now bring the poles with intervening diamond together and form an arc between. The temperature of the diamond rapidly rises, and when it approaches 3600° C., the vaporising point of carbon, it breaks down, swells, and changes into black and valueless graphite. I show this experiment because it is striking and suggestive. I may add that it is costly—because the stone if not of fine quality might easily burst.

And now with this risky experiment my Address draws to a close. I hope I have given you some idea of the underground wonders of the Kimberley mines; my two visits have opened my own eyes. I have tried to picture the strenuous toil of the men who bring to the surface the buried treasures; and I have given you some idea of the skill and ingenuity with which their labours are controlled. I have also given you a sketch of the fiery origin of the diamond, of the glowing, molten, subterranean furnaces where they first take shape. I have shown you that a diamond is the outcome of a series of titanic convulsions, and that these precious gems undergo cycles of strange and potent vicissitudes before they can blaze on a ring or a tiara.

As to myself, I am glad we have made this second journey. I shall always recall with interest the dusky smiling natives at work and at play. And I am glad to have seen that Arabian Nights vision, the strong-room of the De Beers Company, literally heaped with stones ardously won from the blue ground, purified, flashing, and of inestimable price. And, above all, I have vividly graven on my heart the friendly welcome, the innumerable acts of kindness, shown us by our able, energetic, and enterprising Colonial fellow countrymen.

EXAMINATION OF THE COMPARATIVE ABSORPTION OF HYDROGEN BY RHODIUM AND PALLADIUM.

By L. QUENNESSEN.

DURING the course of some researches on metals of the so-called platinum group, I had occasion to check certain properties mentioned by earlier writers.

Thus, according to Th. Wilm (*Berichte*, vol. xiv., p. 629), pure rhodium possesses a capacity for absorbing hydrogen much greater than that of palladium, and this statement is to this day repeated in various text-books. Further, Wilm stated that this property of absorption varies with the method adopted for the preparation of the metal; for example, rhodium obtained by the calcination of the double chloro-ammoniated salt had a greater absorbent power than the metal obtained from the double chloride of sodium or potassium, and that this absorption appeared to be due to a chemical affinity for the metal for hydrogen.

The solution of hydrogen in palladium having been examined by numerous chemists, my object has not been to approach this subject from the physical point of view, but only to compare the absorptive powers of rhodium and palladium for this gas. Now, my experiments in no way confirm those of Wilm.

Rhodium mixed with fused pulverised chloride of sodium was attacked by a current of chlorine at 440° , then, to eliminate the impurities which it might still contain, the product, taken up with pure water, was transformed into the double nitrite of rhodium and sodium (Joly and Leidié, *Comptes Rendus*, vol. cxii., p. 1259). This latter salt was divided into two portions; one treated with hydrochloric acid was brought to the state of double chloride of rhodium and sodium; the other portion was transformed to the state of double chloride of rhodium and ammonium, which was obtained perfectly pure by treating the double nitrite of sodium with chloride of ammonium to form the double ammoniacal nitrite, and then treating this nitrite with hydrochloric acid.

These two compounds were then heated and reduced at a dull red heat in a current of pure dry hydrogen, in which the rhodium sponge was allowed to cool.

In the case of the double salt of sodium we must take care, further, to remove the common salt by washing with warm water, and then repeat the treatment with hydrogen under the same conditions.

If, after complete cooling, we open the tube containing the boat full of rhodium, we observe the formation of water-vapour which condenses on the glass as soon as the metal comes in contact with the air; while if we drive off the atmosphere of hydrogen by means of a current of pure dry carbonic acid, the phenomenon of the formation of water on contact with the air is not produced. Further, if we place the boat of rhodium *in vacuo* and heat to 440° , by the use of a sulphur bottle, the barometer connected to the apparatus shows no variation of pressure, and it is quite impossible to extract the smallest bubble of gas with a mercury pump.

Further, it does not appear that the rhodium obtained from the decomposition of the chloro-ammonia salt has much more active properties than that obtained by the decom-

position of the chloro-soda salt, when this latter has been freed by levigation from the alkaline chloride surrounding it (L. Quennessen, *Comptes Rendus*, vol. cxxxix., p. 795).

On the other hand, pure palladium dissolved in dilute aqua regia was precipitated by chloride of ammonia, and the chloropalladate of ammonium obtained was dried and reduced at a dull red heat by pure dry hydrogen in the same manner as the rhodium salt.

If we let the palladium sponge cool in the current of hydrogen, and then afterwards allow the air to enter the tube containing the metal, we observe the formation of water-vapour which condenses on the sides of the glass.

Under these conditions the phenomenon has been identical up to the present with that observed with rhodium; but if we re-heat and again cool the palladium sponge under the same conditions, and then first drive out the atmosphere of hydrogen by means of a current of pure dry carbonic acid before allowing the air to enter, we again observe on opening the tube an abundant condensation of water-vapour on the glass; as we have already shown, this does not take place in the case of rhodium.

I have even confirmed this production of water immediately on contact of the air with palladium after continuing the current of carbonic gas for an hour and a-half.

These experiments, repeated several times, always gave the same results; we are thus entitled to state that rhodium does not resemble palladium in so far as the chemical affinity for hydrogen is concerned, but that it acts in the same manner as platinum sponge, condensing hydrogen and oxygen to form water.—*Bull. Soc. Chim.*, Series 3, vol. xxxiii., No. 3.

THE ACIDITY OF FRUITS.

By W. F. SUTHERST, Ph.D., F.I.C.

THE apparent increase of acidity in fruits after boiling will have been noticed by most people, the comparative sweetness of raw black currants, for instance, being changed to a mass of rather sour nature after cooking, necessitating the use of considerable quantities of sugar to render it palatable. To see whether acid were possibly formed in the process of boiling, a portion of a mixture of nearly ripe gooseberries and water was boiled for about thirty minutes and titrated with N/1 NaOH. The boiled portion, however, contained less acid than the raw berries, due, no doubt, to the volatility of some of the acids. The next point considered was whether the sugar was inverted or not during boiling. An unboiled quantity of gooseberries contained:—

Cane-sugar	1.16 per cent
Invert sugar	5.84 „

After boiling the mass contained:—

Cane-sugar	0.0 per cent
Invert sugar	6.91 „

Showing that all the sugar undergoes inversion during cooking, the acid present bringing this about as in the usual process of hydrolysis. One other thing noticed in eating raw fruits is that the pulp only is eaten, especially in such fruits as plums, gooseberries, currants, &c., and when the skin and pulp of gooseberries were analysed for acidity they showed the following:—

Skin	2.66 per cent (expressed as tartaric acid)
Pulp	1.80 „ „ „

Now, of course, during the boiling or cooking of fruits, the whole of the acid in the skin is extracted and the semi-liquid mass therefore contains all the acid evenly distributed, whilst if the fruit is eaten raw, and the skin not masticated this extra acidity is not tasted. This latter experiment, perhaps, shows how this phenomenon is brought about.

The Agricultural College, Tamworth.

THE
REDUCTION OF ZIRCONIA WITH MAGNESIUM
AND THE SPONTANEOUS FORMATION OF
ZIRCONIUM NITRIDE.

By E. WEDEKIND.

ZIRCONIUM is one of those elements whose preparation in the pure state presents great difficulties. Of the three allotropic modifications* in which zirconium is said to occur, the crystallised has been the most thoroughly investigated, while the amorphous element has not been further examined since the experiments of Berzelius and Troost; in particular, the conversion of amorphous zirconium into the compact or crystalline modification has not been performed. I hope to be able to report shortly on experiments on this point; the subject of this communication is the reduction of zirconium dioxide by magnesium and aluminium. According to the statements of T. L. Phipson (*cf. Comptes Rendus*, lxi., 745) and the experiments, more recently performed, of Dennis and Spencer (*Journ. Am. Chem. Soc.*, xviii., 673) it must be possible to obtain by the action of magnesium on the oxide, amorphous zirconium, the preparation of which from zirconium potassium fluoride by Berzelius's method is uncertain and inconvenient. Clemens Winkler (*Berichte*, 1891, xxiv., 888; and xxiii., 2664) by heating (two atoms of) magnesium with (one molecule of) zirconium dioxide in a current of hydrogen obtained only a mixture of zirconium hydride, ZrH_2 , and unchanged zirconia; but it was not thereby proved to be impossible that, in the absence of hydrogen, and on using an excess of magnesium and applying a higher temperature, the reaction would proceed as desired according to the equation $ZrO_2 + 2Mg = Zr + 2MgO$.

After the reduction of metallic oxides by means of aluminium according to Goldschmidt's method had rendered possible the preparation of several difficultly fusible metals in the compact condition, an attempt was made to convert the oxide into the free element by the aid of aluminium. It was then found that an intimate mixture of zirconia and aluminium—both granular and powdered metal were used—generally reacted with difficulty and incompletely, the reaction not spreading throughout the whole mass. In some experiments—especially when small quantities were used—a grey mass was obtained which contained relatively little unchanged oxide, but the rise of temperature was in no case sufficient to fuse the elements set free, and thus to render possible its separation from the aluminium oxide simultaneously formed. The product of the reaction, which was freed from excess of aluminium by treating it with dilute acids, consisted of a green crystalline powder, from which, however, the alumina could not be removed on account of its insolubility in acids and alkalis. As the powder, even when strongly compressed, does not conduct the electric current at all, it was impossible to fuse the material and thus purify it with the aid of its own resistance by the method described by me for aluminium zirconide (*cf. E. Wedekind, Zeitschr. f. Elektrochem.*, 1904, 332); nor had heating in the electric furnace had any effect. Thus I was obliged to fall back upon the old method of reducing with magnesium.

According to Phipson (*loc. cit.*, and *Journ. Prakt. Chem.*, [1], xcvi., 448) the reduction of zirconia, which is said to proceed as easily as that of silicic and boric acids, occurs at the moment of the fusing of the magnesium, and the zirconium is obtained in the form of a velvety black powder, from which the magnesia formed is removed by means of dilute hydrochloric acid. No analytical data are given to show that Phipson really had obtained pure elementary zirconium. Dennis and Spencer (*loc. cit.*) worked in an atmosphere of hydrogen, using Winkler's method, with

this modification, that heating in the current of hydrogen was repeated till reduction was as nearly as possible complete. The product contained 80·7 per cent zirconium and 18 per cent oxygen (the residue consisted of small quantities of silicon, magnesium, and hydrogen). Dennis and Spencer are of the opinion that the product of their reaction contained only a little elementary zirconium, and consisted chiefly of zirconium monoxide, ZrO .

I performed the reduction of zirconia as follows:—

The bottom of a crucible* of pure nickel, of height 11 c.m. and diameter 4 c.m., was covered with a thin layer of magnesium powder, upon which was placed an intimate mixture of zirconium dioxide and magnesium powder (40 per cent more than the calculated quantity), and pressed down with a pestle. Magnesium powder was then scattered over the whole. The quantity of the reaction mixture was so measured that the crucible was only one-third filled; it was then covered with a well-fitting cover, and heated before a good blowpipe till the lower part became red-hot; the commencement of the reaction is revealed by hissing, and sometimes the lid is hurled off. At this moment the blowpipe flame is drawn away; the crucible glows for some time longer owing to the heat of the reaction.† After cooling a brownish black powder is obtained, which cakes together and smells distinctly of ammonia; this was then rubbed up under water, and digested at a gentle heat with concentrated ammonium chloride solution in order to remove the excess of magnesium. When the evolution of gas had ceased, warm dilute hydrochloric acid was added till a faintly acid reaction was obtained. After the dark powder had settled, it was twice decanted, filtered, and washed with water; at a definite point in the washing process a part of the product went colloiddally through the filter; the solution was dark blue in transmitted light and greyish opalescent in incident light. It may be mentioned that in a few experiments for some unexplained reason, a colloidal solution of grey-brown colour was obtained. In all cases after repeated washing the colloidal substance in the precipitate was visibly removed; the filtrate ran through perfectly clear; but I noticed that the residue on the filter, the quantity of which had not appreciably diminished, could again be made to yield a colloidal solution, by treating it with warm dilute hydrochloric acid and then washing with cold water; at a definite stage the earlier effect again appeared. If after washing a few times the filtrate again ran through colourless, the process could be repeated. Thus this was a periodic phenomenon, something like Ostwald's solution of chromium in acids. The united colloidal solutions—blue as well as greyish brown—and the residue on the filter were examined separately.

The Colloidal Product Soluble in Water.

The fact that one part of the product of the reduction of zirconia goes into solution in the colloidal form was of importance to me, for I hoped I should be able to obtain this zirconium, which is difficult to obtain pure, for insoluble compounds—especially unchanged oxide—must remain behind in the residue on the filter. It was therefore a question of precipitating the dissolved substance again in a suitable form, and characterising the gel thus obtained as elementary zirconium. But all my efforts in this direction, in spite of many attempts, were fruitless, chiefly because the concentration of the solutions was only exceedingly small, and hence only very little material could be procured. Moreover, it was found that the colloidal solutions‡ could not be made to yield flakes so readily as other colloidal solutions; electrolytes, such as sodium chloride, ammonium chloride, and hydrochloric acid, produce no effect; however, on boiling with hydrochloric acid a turbidity appeared; the fine precipitate thus obtained shows a

* Nickel crucibles of the form described were supplied to me by the Vereinigte Deutsche Nickel Werke in Schwerte. Clay crucibles cannot, of course, be used on account of the presence of magnesium.

† In most cases some part of the nickel crucible fuses.

* The third modification is the graphitic, described by Troost; this is said to result on the decomposition of the compound of zirconia with caustic soda by means of iron, at the temperature of the melting-point of copper; this statement requires confirmation, all the more because iron is a less powerful reducing agent than aluminium or magnesium.

‡ The stability of the solutions varies; most of them after a time deposit a precipitate which does not apparently increase. Also in dialysis experiments flakes were observed clinging to the porous wall.

tendency to go into solution again after being filtered off. A fairly trustworthy precipitant was found in hydrogen peroxide, this being apparently not decomposed by the colloidal substance. On addition of hydrogen peroxide, flakes were slowly formed; the blackish precipitate, which shows a greenish sheen on the surface, may be filtered, but it is difficult to wash it, as it fills up the pores of the filter; fixed alkalis also produce a precipitate. The difficulties of obtaining a preparation sufficiently pure for analysis could not be overcome. A gel, precipitated by hydrochloric acid and afterwards dried in the desiccator and at 100° , was converted into colourless zirconium dioxide by heating in a platinum crucible:—

0.3326 grm. of the substance gave 0.3429 grm. ZrO_2 (pure elementary zirconium would have yielded 0.4499 grm. of oxide).

A preparation precipitated with hydrogen peroxide behaved similarly:—

0.4487 grm. of the substance gave 0.44935 grm. of ZrO_2 .

Many preparations could not be brought to constant weight, as the moisture in the gel did not escape completely at the temperature in question. When such a preparation was heated *in vacuo*, on the cold part of the tube it was possible to see not only a deposit of moisture, but also a yellowish white sublimate. A specimen of a preparation thus treated gave on ignition not an increase but a small decrease of weight:—

0.2281 grm. of the substance gave 0.2194 grm. ZrO_2 .

The chemical nature of the colloiddally dissolved substance could not be established; from its behaviour on being heated in rarefied air it was probably an adsorption compound of zirconium or zirconium nitride with zirconium oxychloride,* and it seems probable that the grey-brown colloid is zirconium itself, as Berzelius (*cf. Pogg. Ann. d. Phys. u. Chem.*, 1825, iv., 121) has already observed that his amorphous zirconium gave in pure water a dark brown colour, which appeared dark grey in reflected light. The blue colloid might then be regarded as the absorption compound of zirconium nitride (see below).

The colloidal nature of the solution in question was proved by its behaviour under the electrical potential gradient; for this purpose a U-shaped glass tube was used, platinum discs of about 10 m.m. diameter being employed as electrodes;† a sensitive ampère meter and potentials of 24–104 volts were also used. Although the solutions were rendered faintly acid with hydrochloric acid, the conductivity was small, as the following table shows:—

Grey-brown Colloid.;

Potential, in volts.	No. of mill.-amps.	Resistance, in ohms.
24	4	6000
68	13	5200
104	14	7400
104	17	6100

The phenomena observed were the same with all potentials; the cathode was soon covered with a fine black deposit, and had the appearance of a platinised electrode; in the neighbourhood of the cathode the flakes were thickest. When the current was commuted the strength of the current rose for a moment to 24 mill.-amps. The electrode covered with the black deposit soon became clean again, while the other one blackened. The flaking was only incomplete. On using a very dilute perfectly transparent solution the formation of black clouds could be plainly observed; these migrated to the cathode. No sudden flaking took place. In this case with a potential of 104 volts 4 mill.-amps. went through the liquid, corresponding to a resistance of 26,000 ohms. The electrolysis was in all cases very feeble.

* This is confirmed by the coagulation by alkalis, which decompose the oxychloride, when the colloid is brought down.

† The electrodes were about 6.5 c.m. apart.

‡ The blue colloid behaves perfectly analogously.

The dissolved particles thus migrate to the cathode; this discovery was surprising, because Whitney at the meeting of Section X. of the International Congress for Applied Chemistry (Berlin, 1903) had reported (*cf. Zeit. f. Elektrochem.*, 1903, ix., 633) that colloidal zirconium under the influence of an electric potential gradient migrates in the direction of the negative current, like colloidal platinum and many other simple substances. As Whitney had given no information about the preparation of this colloidal zirconium, I asked for a private communication on the subject. Mr. J. E. Ober, Prof. Whitney's collaborator, was then kind enough to place the information at my disposal. The material used for the experiments was prepared by the action of magnesium on zirconium tetrachloride, and purified in the same way as my reduction product, but a perfectly neutral solution of the colloid was obtained, otherwise resembling my (blue) preparation. The transport experiments were so arranged that electrolytic products of decomposition could not reach the colloid; the latter was attracted by the positive electrode. There was no analytical proof of the elementary nature of the colloidal substance. Ober also investigated the reduction of zirconia with magnesium, and the product obtained by him corresponds approximately to the composition of a suboxide, ZrO , as well as the black colloid obtained at the same time. It is clear that the question of the nature of the colloidal reduction products of zirconium dioxide with magnesium presents greater complications than was to be expected, and requires further investigation."

Finally, as regards the cause of the periodic phenomenon on the formation of the colloidal reduction product (see above) I am inclined to agree with an opinion expressed by G. Bredig, namely, that when magnesium acts upon zirconia, first an alloy or compound of zirconium with magnesium is formed, and is then destroyed by acids, when the zirconium or the nitride remains behind in the colloidal state (*cf. Zeit. f. Elektrochem.*, 1903, ix., 631; Discussion on the lecture "Colloidal Zirconium," in Section X of the International Congress for Applied Chemistry, 1903). If we assume that this process is stopped in consequence of partial inclusion of the alloy in insoluble substance, and is set going again by contact with fresh acid, the periodicity of the process would be explicable up to a certain stage.‡ Such periodic phenomena have been occasionally observed in electrolytic processes, e.g., in the electrolysis of sodium carbonate with mercury electrodes according to Arrhenius (*Zeit. Phys. Chem.*, 1893, xi., 805); also with lead at high current densities, and with lead-sodium if it is chemically attacked (*cf. Bredig and Haber, Berichte*, 1898, xxxi., 2741; Haber and Sack, *Zeit. f. Elektrochem.*, 1902, viii., 251; M. Reuter, *Ibid.*, viii., 801; and Sack, *Zeit. Anorg. Chem.*, 1903, xxxiv., 286).

In agreement with observations from other sources (*cf.*, among others, E. Jordis and E. H. Kanter, *Zeit. Anorg. Chem.*, 1903, xxxv., 21) it appears that in the case described certain small impurities—chiefly zirconium oxychloride (see above) and perhaps some zirconium hydride—favour or even render possible the formation of the colloidal substance.

The Insoluble Residue (Zirconium Nitride).

The residue remaining on the filter after washing the colloid forms a brownish green crystalline powder, which appears under the microscope like a magma of bronze-coloured small crystals with a faint greenish surface sheen. On gently heating‡ in the air it forms colourless zirconia,

* The fact that the dissolved particles in the solutions obtained by me migrate to the cathode and are thus positively charged, seems to me to argue against their elementary nature, for most colloidal elementary substances migrate in the direction of the negative current.

† As the substance was well rubbed up before the treatment with hydrochloric acid, it was to be expected *a priori* that any magnesium zirconide present would be completely decomposed by the excess of acid employed.

‡ The nitride burns with glittering sparks on being sprinkled in a flame.

but is otherwise of remarkable stability both towards acids—with the exception of hydrofluoric acid—and towards alkalis; even when it is boiled for some time with the latter no ammonia is evolved. If, however, the substance is introduced into fused caustic alkali, when a feeble luminescence phenomenon is to be observed the presence of nitrogen is revealed by a distinct ammonia reaction. The combined nitrogen may also be demonstrated as such if the nitride is oxidised in an atmosphere of carbon dioxide, and the nitrogen thus set free is collected. For this purpose weighed quantities of the substance were mixed with fine granular copper oxide, and, as in nitrogen determinations in the case of organic substances, burnt in a tube of difficultly fusible glass containing a reduced copper spiral; the gas evolved was collected in an azotometer over caustic potash, and measured:—

- I. 0.4025 grm. of the substance gave 31 c.c. of nitrogen at 20° and 731 m.m. pressure, corresponding to 8.47 per cent N.
- II. 0.5533 grm. of the substance gave 41 c.c. of nitrogen at 16° and 743 m.m. pressure, corresponding to 8.3 per cent N.

An attempt to determine the nitrogen in the potash melt quantitatively as ammonia failed, owing to experimental difficulties.* The increase of weight on converting it into zirconium dioxide was therefore determined. A specimen of the raw product gave the following number:—

- 0.8819 grm. of the substance gave, after ignition to constant weight, 0.8972 grm. ZrO_2 (increase of weight, 0.0153 grm.). A preparation purified by washing with bromoform gave a number agreeing with the theory for the nitride, Zr_2N_3 .
- 0.8752 grm. of the substance gave 0.9632 grm. ZrO_2 (observed increase of weight, 0.088 grm.; calculated for Zr_2N_3 , 0.086 grm.). Calculated for Zr_2N_3 ; Zr , 81.2; found Zr , 81.35.

Matthews (*cf. Journ. Am. Chem. Soc.*, 1898, xx., 843) prepared two zirconium nitrides, Zr_2N_8 and Zr_2N_3 , by another method—by heating zirconium chloride ammonia; the product obtained by me from zirconia appears to consist essentially of the nitride, Zr_2N_3 . In order to see whether the difference in the nitrogen result is due to the presence of unchanged zirconium oxide, in another experiment the latter was determined by dissolving the substance in concentrated hydrofluoric acid, collecting the insoluble residue on a small filter,† and igniting. The filtrate was evaporated to dryness, moistened with concentrated sulphuric acid, and ignited to constant weight. 0.3868 grm. of the substance left an insoluble residue of 0.0156 grm. ZrO_2 , and gave, after conversion into the oxide, 0.4105 grm. ZrO_2 .

The preparation in question therefore contains 3.52 per cent unchanged or regenerated zirconium dioxide; after subtracting this the zirconium percentage works out to 81.31 per cent. (Theoretical amount for Zr_2N_3 , 81.2 per cent Zr).

The amount of zirconia is thus not great enough to explain the deficiency of nitrogen. We are therefore forced to conclude that the zirconium nitride mixed with the copper oxide is only incompletely burnt on heating in an atmosphere of carbon dioxide. As a matter of fact, in the potash melt a portion of the substance remains dark coloured, and thus seems to escape decomposition.

The zirconium nitride resulting on the reduction of zirconia in the air is attacked readily, not only by oxygen, but also by chlorine, forming zirconium tetrachloride at a faint red heat. The yield is certainly not satisfactory, but at any rate we have here a method of quickly and conveniently preparing small quantities of this chloride, which is otherwise not easily obtained. The nitride becomes luminescent on being heated with bromine vapour, and the

preparation of zirconium tetrabromide—especially on the small scale—is thus performed very simply: zirconium oxide is first converted into the nitride as described above, and the latter, on being heated with bromine in a test-tube, gives a crystalline sublimate of zirconium bromide, fuming in the air.

The nitride is remarkably stable towards concentrated nitric acid, even on heating, and also towards aqua regia. In the form of a pressed powder, the compound does not conduct the electric current.*

The tendency to form zirconium nitride must be fairly great, for even by acting with magnesium on zirconia in a rarefied space—using an iron tube—a crystalline powder is obtained; this powder, on oxidation, exhibits only a slight increase of weight. Since, when aluminium is used, the formation of zirconium nitride decreases very much, it must be supposed that the magnesium nitride first resulting from the excess of magnesium† functions as a nitrogen carrier, and promotes the formation of zirconium nitride.

Finally, it must be emphasised that no support has been found for the existence of a divalent zirconium compound—the long-sought zirconium monoxide, ZrO . In agreement with the experimental results of Cl. Winkler, it has been found that zirconia cannot be completely reduced by magnesium. Moreover, it appears that the nitrogen of the air readily takes a direct or indirect part in the reaction, and causes the formation of the difficultly saponified but easily oxidised zirconium nitride. The statement of Phipson (see above), who claims to have obtained elementary zirconium by the action of magnesium on zirconia, cannot be checked, owing to the lack of further information and analytical data, but most probably Phipson had obtained only zirconium nitride or a mixture of it with zirconium.—*Zeit. Anorg. Chem.*, 1905, xlv., 385.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY OF NEW SOUTH WALES.

General Monthly Meeting, July 5th, 1905.

H. A. LENEHAN, F.R.A.S., President, in the Chair.

MR. W. A. DIXON, by permission of the President, made the following remarks:—

He had often found that young men were quite willing to work out any investigation, but that they were not aware of any subject which would repay them; he therefore desired to suggest one in which he had found no information. He thought it deserved investigation, but had no time himself to attempt it. He had in his dining-room a Fletcher's gas-fire, an upright fire-clay block, with tufts of asbestos heated to radiation of heat point by a Bunsen flame. Some years ago, sitting in front of this, it occurred to him that it would be an improvement to convert the colourless flame to a coloured one, and therefore twisted some wires into a rope and saturated this with brine to obtain a sodium flame. Next night, the fire having got hot, he introduced the saturated wire at the base of the flames, and immediately found a great reduction in the radiation, so that he felt quite cool. Removal of the wires and re-insertion several times always produced the same effect.

The subject he had to suggest was, therefore, "The radiation from coloured flames." To this might very well be added the absorption of radiant heat by coloured glass which varies much. In this part it would be necessary to

* The filament of the new zirconium lamp (D.R.P. 137201 and 137569) consists of a mixture of compounds of zirconium with nitrogen, hydrogen, and carbon, to which rhodium is also added in order to obtain the necessary conductivity.

† On using the calculated quantity of magnesium, in one experiment a grey crystalline powder was obtained, which did not appear to be identical with the zirconium nitride investigated.

* Complete decomposition requires temperatures which the material of the vessel will not stand.

† Ignited zirconium oxide is practically insoluble in hydrofluoric acid.

use coloured glass of standard light penetration, such as is used in Lovibond's tintometer.

Remarks were made by Dr. F. H. Quaife and Mr. G. H. Knibbs.

The following paper was read:—

"Observations on the Illustrations of the Banks and Solander Plants." By J. H. MAIDEN, Government Botanist, and Director of the Botanic Gardens, Sydney.

The issue of the third and final volume and plates, from the coppers engraved in the Eighteenth Century from drawings by Nodder, Cheveley, and the two Millers, prepared under the direction of Banks, and depicting over 400 plants collected by him in 1770 during Cook's first voyage, is—to Australians at least—an important historical event, which assuredly demands the most marked emphasis that Australians can give it.

The present work has been written by Mr. James Britten, of the British Museum, with the authority of the trustees of that institution. Many of Banks' plants depicted were presented by the trustees to the National Herbarium, Sydney. The scope of this work is explained, and the proposed changes in nomenclature are indicated and compared with the names in the "Flora Australiensis."

This handsome publication, apart from its historical value, is a notable addition to existing iconographies of Australian plants.

Remarks were made by Messrs. W. J. Clunies Ross, R. T. Baker, W. M. Hamlet, and the author.

General Monthly Meeting, August 2nd, 1905.

The following paper was read:—

"The Refractive Indices, with other Data, of the Oils of 118 Species of Eucalyptus." By HENRY G. SMITH, F.C.S., Assistant Curator, Technological Museum, Sydney.

In this paper the author records the refractive index, the specific gravity, the specific refractive energy, and the solubility in alcohol of the oil of each species. The material was distilled at the Museum, and most of it had been prepared for the work "Research on the Eucalypts and their Essential Oils," by Mr. R. T. Baker and himself, so that it was of undoubted origin. The oils of those species which have been obtained since that work was published are also included. By working upon the oils of such a large number of species it was possible to arrange the results in some order. The specific refractive energy results cannot be used to any great extent for the purpose of classification, but if the refractive index be multiplied by 10 times the solubility in 70 per cent alcohol (sp. gr. 0.8722 at 15.5° C.) a very good arrangement of the eucalyptol oils can be made. Those oils which contained eucalyptol in excess had, as a rule, the least refractive index, and were the most soluble in alcohol. As the pinene increased in amount the solubility diminished, and although the refractive index remained much the same, yet the resulting figures increased considerably. The solubilities were taken in tenths, and the temperature for all the determinations was 16° C. The oils of the 51 species in the eucalyptol group had refractive indices ranging from 1.4686 to 1.4774, and the solubility was from 1.05 to 8 volumes 70 per cent alcohol, down to No. 45, the remaining six being insoluble in 10 volumes. The specific gravities of the oils of this group were mostly above 0.9. The 7 pinene oils in which phellandrene was absent had refractive indices ranging from 1.4741 to 1.4788, and none were soluble in less than 7 volumes 80 per cent alcohol. The pinene oils (14 species) in which the sesquiterpene was pronounced, and phellandrene absent, had refractive indices ranging from 1.4801 to 1.4948, while the oils which contained the aldehyde aromadendral in some quantity, and in which phellandrene was absent (9 species), had refractive indices from 1.4828 to 1.4946. The refractive indices of the phellandrene oils which contained piperitone (11 species) ranged from 1.4828 to 1.4945. The 22 phellandrene oils in which the sesquiterpene was

a pronounced constituent had refractive indices ranging from 1.4801 to 1.5065. The perfumery oils, as *E. citriodora*, *E. macarthurii*, and *E. Staigeriana*, were not classified.

Remarks were made by Mr. W. A. Dixon, Mr. W. M. Hamlet, Dr. George Harker, and Mr. G. H. Knibbs. The author replied.

NOTICES OF BOOKS

The Synthetic Dye-stuffs and the Intermediate Products from which they are Derived. By JOHN CANNELL CAIN, D.Sc. (Manchester and Tübingen), and JOCELYN FIELD THORPE, Ph.D. (Heidelberg). London: Charles Griffin and Company, Ltd. 1905.

This work will probably soon be regarded as invaluable both by technical students and by dye-works chemists. It is exceedingly practical, and possesses the great advantage of advocating the use of only such reagents as would in all probability be found in a works laboratory, and, moreover, it describes only those quick and simple methods which are actually the best to be employed technically, and not those which are of scientific interest only. The book is divided into three parts. The first gives theoretical descriptions of the various intermediate products and dye-stuffs, and shows very clearly the structure, reactions, and transformations of the various classes of dyes. The second part describes the methods of preparation of the more important intermediate products and dye-stuffs, concise directions being given for their preparation on the small scale, and short notes on such of their properties as the student should investigate for himself experimentally, while the last part details the methods of identification of the same substances, the valuation of colouring matters and their application, and in fact all that is likely to be required of a chemist in the way of analytical investigation. The importance of a thorough knowledge of the theory of dyeing is rightly emphasised, and every facility is given for the student to acquire such knowledge and to enable him to apply it intelligently in practice. It is difficult to see how the plan the authors have adopted could be improved upon, and no better book could be recommended, more especially for the use of technical students.

Premature Burial and How it may be Prevented. By WILLIAM TEBB, F.R.G.S., and COL. EDWARD PERRY VOLLUM, M.D. London: Swan Sonnenschein and Co., Ltd. 1905.

THE second edition of this work has been slightly enlarged and brought up to date by Dr. Walter R. Hadwen, who has added new cases of importance to the gruesome list which the original authors had compiled and annotated. According to the authors a certain amount of reticence has been shown in not including the most horrible cases on record, and for this they are much to be commended; in so doing they have not weakened their case in favour of legislation in the way of altering the present law as regards the delay of burial till the one unmistakable sign of death has ensued, the giving of death certificates, and the provision of waiting mortuaries similar to those already in use on the Continent.

Die Elektrolytische Chloratindustrie. ("The Electrolytic Chlorate Industry"). By JOHN B. C. KERSHAW, F.I.C. Halle-a-S.: Wilhelm Knapp. 1905.

THE author of this monograph, which forms the nineteenth volume of the series of monographs of applied electrochemistry, has had many difficulties to contend with in collecting his material, the chief being due to the unwillingness of manufacturers to give details of the works under their control. This secrecy is always a marked feature of the beginnings of an industry, and in this case it accounts for the lack of information regarding plant and cost of working to be found in the book. However, the author has done his utmost with the material at his disposal, and

has produced a very useful monograph. He outlines the growth of the industry from its earliest beginning, and as he is of the opinion that it is best to study thoroughly the work of the earlier investigators, he includes descriptions of processes which may now be regarded as superseded. While this plan of tracing the development of the industry undoubtedly leads to the production of a most interesting work, it appears doubtful whether it is altogether advisable when the space at the disposal of the author is limited, and it would probably be best to follow the mean course between this plan and that of neglecting all early work altogether. The book has been ably translated into German by Dr. Max Huth.

La Chimie Minérale, Ses Relations avec les Autres Sciences. ("Mineral Chemistry and its Relations to the other Sciences"). By HENRI MOISSAN. Paris: G. Steinthal. 1904.

This lecture, delivered before the Congress of Arts and Sciences at the Exhibition at St. Louis in September, 1904, gives a short historical account of the developments of inorganic chemistry from the earliest times, and of the assistance it renders towards the solution of the problems of other sciences. As regards the fusion of physics and chemistry, the recent advances made by the aid of spectrum analysis, and of electrolytic processes and the production of high and low temperatures, all provide the author with subjects of which to give graphic accounts. He also discusses briefly the connections between biology, astronomy, mathematics, and geology and chemistry, the whole lecture being full of suggestion and most stimulating reading.

CORRESPONDENCE.

INSTITUTE OF CHEMISTRY EXAMINATIONS.

To the Editor of the Chemical News.

SIR,—I have read with much interest the article on the Scheme for Examinations in Technical Chemistry in connection with the Institute of Chemistry (CHEMICAL NEWS, vol. xcii., p. 155).

Some scheme of this nature is very much needed, but at the same time if the exact lines denoted in the article are strictly followed, a great number of works chemists will still be debarred from the advantages, because of Clause 2, which states that the "examinations will be open only to Fellows, and to those Associates who have been registered as such for at least one year."

There are many chemists employed in technological work who have never had the opportunities and advantages which are necessary to become A.I.C. or F.I.C.; that is, have not been able to attend colleges recognised by the Institute, &c., and still who could produce evidence of good general education, and Honours Certificates from the Board of Education in several subjects probably, relating more particularly to their own sphere of work.

In my opinion, the scope of usefulness of the proposed scheme would be much widened if an extra conditional clause be inserted therein to the effect that candidates satisfying certain conditions, based on some such considerations as the above, be admitted to the examinations in technical chemistry.

While dealing with this subject I may say that a kindred matter has often occupied my thoughts with regard to the Board of Education and City and Guilds of London certificates. A person holding Honours Certificates granted by these bodies has absolutely no "status" compared with a B.Sc., A.I.C., or F.I.C. Is it not time that this was remedied, and that some kind of degree or distinction be associated with these diplomas? Surely they are worth it.

In the hope that this letter may induce others to state their views on the subject, and ventilate the question generally, I am, &c.,

TECHNICUS.

VON KOBEL'S TEST FOR BISMUTH.

To the Editor of the Chemical News.

SIR,—In performing the test for bismuth known as Von Kobel's, it occurred to me to try whether any other metals gave similar results. I then found that arsenic and antimony both gave red sublimate when treated with this reagent on aluminium plate.

The arsenic reaction was quite as delicate as the bismuth, and the red was much lighter and faded off to a lemon-yellow. The antimony reaction was less delicate, and in quantity resembled the bismuth.

As these results do not appear in any of the standard works, perhaps some of your readers may be interested in them.—I am, &c.,

D. E. RAMSEY.

80, Elspeth Road, Clapham Common, S.W.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 10, September 4, 1905.

Constitution of Copper-aluminium Alloys.—Leon Guillet.—The author's investigations on the subject of the copper-aluminium alloys show the presence of seven constituents:—1. A solution containing 0 to 8 per cent of aluminium; this constituent has often been confused with the constituent Cu_3Al . 2. The compound Cu_3Al or a solid solution of this. 3. A solid solution which is produced during tempering. 4. A solid solution in which the proportion of aluminium varies between 14 to 30 per cent. 5. The compound Al_2Cu . 6. A compound similar to Al_2Cu , but not quite identical. 7. Either pure aluminium or an aluminium-copper solution containing a very small proportion of copper. It is probable that there also exists a solution containing 44 to 46 per cent of aluminium.

MISCELLANEOUS.

New Zealand International Exhibition.—The Government of New Zealand has decided to hold an International Exhibition during the summer of 1906-7, at Christchurch, Canterbury, New Zealand, in which all nations of the world have been invited to participate. The object of the Exhibition is educational, and it is intended to demonstrate the resources and possibilities of the Colony as one of the world's food-producing factors, its vast mineral resources, and to draw attention to its unrivalled and varied scenery, thermal wonders, and the exceptional opportunities offered to sportsmen. It is further intended to bring under the notice of the more industrial nations of the world the great field the Colony of New Zealand offers as an outlet for enterprise, and for the use and consumption of all manner of up to date appliances, manufactures, &c. As a food-producing country it is only necessary to instance the rapid growth of the development of the New Zealand frozen meat industry, and the dairying industry, which is still only in its infancy. New Zealand's mineral wealth is shown by the continuous and increasing output of gold, which, in the past fifty years, has totalled £65,000,000 in value. There are also large deposits of coal, iron-sand, and iron-ore in the Colony. Further particulars may be obtained from the Secretary of the Local Committee, Christchurch, New Zealand.

THE CHEMICAL NEWS.

VOL. XCII., No. 2394.

ON THE THERMO-ELECTRIC JUNCTION AS A MEANS OF DETERMINING THE LOWEST TEMPERATURES.*

By Sir JAMES DEWAR, M.A., D.Sc., LL.D., F.R.S.

THE inconvenience of using the gas thermometer at very low temperatures and the failure of platinum and other metal resistance thermometers within 30° or 40° of the absolute zero, led me some years ago to consider the experimental behaviour of the thermo-electric junction at the lowest temperatures. My special object at the time the experiments were made was to have a further confirmation of the melting-point of hydrogen, and also of the lowest temperature reached on exhausting solid hydrogen, other than that I had found by means of the hydrogen gas thermometer ("The Boiling-point of Liquid Hydrogen, Determined by Hydrogen and Helium Gas Thermometers," *Proc. Roy. Soc.*, 1901, vol. lxxiii.). The results have remained unpublished, because my intention has always been to extend them to other thermo-electric combinations. Not having been able to accomplish this project, they are now abstracted as affording useful information in this field of investigation, and as furnishing a general confirmation of my previous investigations.

A German-silver platinum couple was selected as likely to give the most uniform results at low temperatures, although subsequent experiments have led to the conclusion that it would have been better to have replaced the platinum by gold. As regards resistance thermometers, I have shown that gold is more reliable than platinum at temperatures near the boiling-point of hydrogen (Bakerian Lecture, "The Nadir of Temperature and Allied Problems," *Proc. Roy. Soc.*, 1901, lxxviii.). The difficulties of the investigation were considerable; it had to be carried out at the time in the neighbourhood of the machinery producing the liquefied gases required in the investigation—namely, oxygen, nitrogen, and hydrogen—so that the zero of the delicate galvanometer employed did not remain quite constant. To remedy this I inserted a rocking make-and-break in order to get the readings of each observation at both ends of the scale. In the process of removing one difficulty another presented itself, through the development of small but appreciable thermo-electric currents in the rocker. Precautions had to be taken against these, and at all other metal junctions against similar small thermo-electric currents, and it was even found necessary to have a correction on account of the resistance box inserted in the circuit to bring large readings within the limits of the scale. The galvanometer and resistance box were inserted in the German-silver branch of the couple, the points of junction of the copper leads with the German-silver ends of the couple being insulated and placed close together within a vacuum test-tube packed with cotton-wool to ensure equality of temperature.

Preliminary experiments showed that the junctions altered after having been subjected to the temperature of liquid hydrogen. However, on resoldering the junctions with hard silver solder instead of soft solder, the thermocouple accurately repeated observations at the temperature of liquid oxygen, after having passed through a liquid hydrogen bath. From this it appears that all such couples before calibration ought to be cooled suddenly in liquid air and then rapidly heated to the ordinary temperature, a similar operation being repeated with liquid hydrogen. If the couples return to their original state after such abrupt changes of temperature, then they are in a fit state for calibration.

Three series of observations were made to determine whether the resistance of the junctions varied to a noticeable extent with the temperature, namely, at the freezing-point of water, at the boiling-point of oxygen, and at the boiling-point of hydrogen. Six very concordant observations with varying resistances in the resistance box were made between 0° C. and 15° C. These were reduced by the method of least squares, and gave for the resistance of the circuit 3,500 ohms. Five similar results between the melting-point of nitrogen and the boiling-point of oxygen gave, by least squares, 3,293 ohms. Only two observations were taken in liquid hydrogen, which are therefore not entitled to the same weight as those already given, but the resistance appeared again about 3,3 ohms. As the variation of the resistance of the circuit was so slight, an attempt was made to reduce the results on the assumption of constancy, but this was not satisfactory. However, on treating the variation of the resistance of the circuit as linear with the temperature, the data came into better agreement.

Table I. contains the details of the observations made with the silver soldered German-silver platinum couple, the recorded readings of the galvanometer being the means of several observed readings, corrected when necessary for resistance introduced into the circuit.

TABLE I.

No. of expt.	Substances used for difference of temperature.	Corresponding absolute temperatures.	Mean absolute temperature.	Mean galvanometer reading.	dE/dt .
1.	Water at 15° and ice	$280^{\circ}, 273^{\circ}$	280.5°	463.2	30.88
2.	Boiling carbonic acid and ethylene	195, 170	182.5	693.5	27.74
3.	Boiling ethylene at 10 m.m. and oxygen	$123.5, 90.5$	107	724.0	21.94
4.	Boiling oxygen and nitrogen	$90.5, 77.5$	84	279.0	21.46
5.	Boiling nitrogen and melting nitrogen	$77.5, 62.5$	70	320.7	21.38
6.	Boiling hydrogen and melting nitrogen	$62.5, 20.5$	41.5	623.5	14.84
7.	Boiling hydrogen and melting hydrogen	$20.5, ?$	$?$	51.0	$?$
8.	Boiling hydrogen—solid hydrogen about 20 m.m. . . .	$20.5, ?$	$?$	64.0	$?$

dE/dt is the quotient of the mean galvanometer reading by the difference of the temperatures in the third column.

On plotting the first six of these results, the first, second, and sixth and means of the other three—viz., $dE/dt = 21.59$ at $t = 87^{\circ}$ —lie nearly on a continuous curve (Fig. 1). The continuity of the curve, without any approach to abrupt change of form, even in the region of liquid hydrogen, shows that a silver soldered German-silver platinum couple is an efficient instrument for the determination of the lowest temperatures hitherto reached. For example, we may employ the curve (Fig. 1) to determine the temperature of the hydrogen under exhaustion in observation No. 8. A graphical examination of the curve in the neighbourhood of the boiling-point of hydrogen shows that we may write—

$$dE/dt = 10.2 + \frac{1}{2}(t - 18), \text{ or } dE/dt = 7.2 + \frac{1}{2}t,$$

as an equation holding true for a few degrees above or below 18° absolute. Hence, if x be the required temperature, we have—

$$\frac{64}{20.5 + x} = 7.2 + \frac{20.5 + x}{12} \text{ or } 20x^2 + 172.8x = 28469,$$

one of whose roots is 14.15 . From the graphical analysis

* A Paper read before the Royal Society, June 8, 1905.

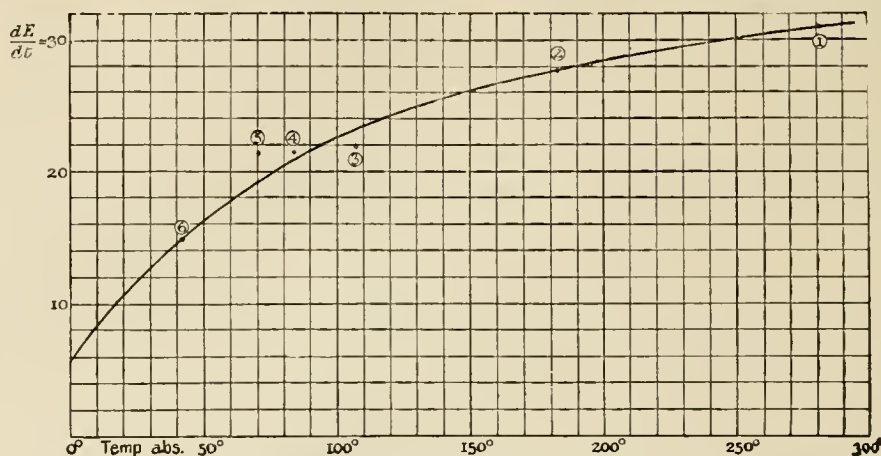


FIG. 1.—THERMO-ELECTRIC JUNCTION.

of the curve, therefore, we find the temperature of the hydrogen under exhaustion in the last observation to be 14.15° absolute, or some 6.3° below the boiling-point. Similarly, for observation No. 7 the temperature is found to be 15.50° .

From the results a curve with electromotive force, E , as ordinate, to absolute temperature, t , as abscissa, may be drawn, and this may be taken as a parabola, with the equation—

$$(t+a)^2 = p(E+b) \quad \dots \quad (1).$$

For another point, t' , E' , we have—

$$(t'+a)^2 = p(E'+b),$$

whence, subtracting,—

$$E' - E = p^{-1} (t' - t) (t' + t + 2a) \quad \dots \quad (2).$$

Any pair of observations will give p and a , after which, assuming any given point, for example H_{BP} , as origin, and putting $t = 20.5^\circ$ absolute and T for $t' - 20.5$, we get the equation connecting difference of electromotive force and difference of temperature—

$$E' - E = p^{-1} T \{T + 2(t+a)\}.$$

An average value of dE/dt from (2) is equal to $\frac{E' - E}{t' - t}$, that is $p^{-1} (t' + t + 2a)$; but the correct value of dE/dt at a given point is, from (1),—

$$\frac{dE}{dt} = \frac{2}{p} (t+a).$$

Now the fact that the Tait line does not remain straight, but bends downwards as we approach the absolute zero, indicates that the parabola is being distorted as we approach its vertex, just as if the vertex were being pushed up. To look for a straight line near the vertex therefore we must keep to observations near the vertex. I have therefore taken the four sets, Nos. 3, 4, 5, 6, from the table, similarly marked on the diagram (Fig. 2), in which the highest extends from ethylene exhausted, 123.5° absolute, to the boiling-point of oxygen, 90.5° absolute.

These corrected observations are given in Table II.

TABLE II.

Range.	Temp. abs.	$E' - E$.	$t' - t$.	$t' + t$.
(3). Ethylene exh. to boiling oxygen..	$123.5 - 90.5$	724.0	33	214
(4). Boiling oxygen to boiling nitrogen.	$90.5 - 77.5$	279.0	13	168
(5). Boiling nitrogen to melting nitrogen	$77.5 - 62.5$	320.7	15	140
(6). Melting nitrogen to boiling hydrogen	$62.5 - 20.5$	623.5	42	83

Hence equations of form (2), re-arranged more conveniently for calculation are—

$$(3). \quad 33 \times 214 + 2a.33 = 724 \quad \text{or} \quad 214 + 2a = 21.9\bar{p}.$$

$$(4). \quad 13 \times 168 + 2a.13 = 279 \quad \text{,,} \quad 168 + 2a = 21.5\bar{p}.$$

$$(5). \quad 15 \times 140 + 2a.15 = 320.7 \quad \text{,,} \quad 140 + 2a = 21.4\bar{p}.$$

$$(6). \quad 42 \times 83 + 2a.42 = 623.5 \quad \text{,,} \quad 83 + 2a = 14.8\bar{p}.$$

Taking (3) and (6), we get $p = 18.45$ and $2a = 190.0$. Therefore $E = \frac{1}{18.45} T (T + 231)$, reckoning from H_{BP} as origin. Hence for $E = -51$ we have—

$$(T + 115.5)^2 = 115.5^2 - 51 \times 18.45 = 111.4^2.$$

Therefore $T = -4.1$, or H_{MF} is 4.1° below H_{BP} , or is 16.4° absolute.

For $E = -64$, $T = -5.23$, or $H_{exh.}$ is 5.23° below H_{BP} , or is 15.27° absolute.

From (3) and (6), reckoning from H_{BP} as origin, we get—

$$dE/dt = 12.52 + 0.108T.$$

There is hardly a doubt that dE/dt at H_{BP} is not so great as 12.52 , so that, as was anticipated, the $E_{thexh.}$ — O_{BP} observations are too far away from H_{BP} to give a workable formula.

Taking (4) and (6) we get $p = 12.69$ and $2a = 104.8$.

Therefore $E = \frac{1}{12.69} T (T + 145.8)$, reckoning from H_{BP} as origin. Hence for $E = -51$ we have—

$$(T + 72.9)^2 = 72.9^2 - 51 \times 12.69 = 68.3^2.$$

Therefore $T = -4.6$, or H_{MF} is 4.6° below H_{BP} , or is 15.9° absolute.

For $E = -64$, $T = -5.8$, or $H_{exh.}$ is 5.8° below H_{BP} , or is 14.7° absolute.

From (4) and (6), reckoning from H_{BP} as origin, we get—

$$dE/dt = 11.49 + 0.158T.$$

In like manner from (5) and (6) we get $p = 8.64$ and $2a = 44.8$, whence $E = \frac{1}{8.64} T (T + 85.8)$, reckoning from H_{BP} as origin.

For $E = -51$ we get $(T + 42.9)^2 = 42.9^2 - 51 \times 8.64 = 37.4^2$, and therefore $T = -5.5$, giving the melting-point of hydrogen 5.5° below its boiling-point, or 15.0° absolute; and when $E = -64$, $T = -7.0$, or the temperature of the hydrogen under exhaustion was 13.5° absolute. Observations (5) and (6) also lead to the equation—

$$dE/dt = 9.931 + 0.231T,$$

with the boiling-point of hydrogen as origin of temperature.

It is of importance to examine how an alteration of any

of the constants in the formulæ employed affects the temperature deduced.

Choosing any assigned temperature as origin, the value of dE/dt at T° from that origin is given by an equation of the form $dE/dt = m + nT$.

But if the value assigned to dE/dt is obtained by dividing the difference of electromotive force D through the range of temperature T by T , then this value of dE/dt must be assigned to the mean temperature $\frac{1}{2}T$, and the formula becomes—

$$D/T = m + \frac{1}{2}nT, \text{ or } D = mT + \frac{1}{2}nT^2,$$

a quadratic for the determination of T when D is known.

When the constant n alone varies, differentiating we have—

$$dT = -\frac{1}{2} \frac{T^2}{m + \frac{1}{2}nT} dn.$$

Thus if $m = 9.931$, $n = 0.231$, and $T = -7^\circ$, we get—

$$dT = -\frac{49}{16.628} dn = -2.947 dn;$$

hence for $dn = -0.031$, $dT = +0.101$, showing that an

alteration of n from 0.231 to 0.200 would only alter T from -7.0° to -6.9° ; or, roughly, a 10 per cent change in n at this temperature would only affect the temperature by 1 per cent.

When the constant m alone varies, differentiating we have—

$$dT = -\frac{T}{m + \frac{1}{2}nT} dm;$$

hence, in the same circumstances as before,—

$$dT = -\frac{7}{8.314} dm = 0.842 dm;$$

and thus, for a change $dm = 0.119$, the corresponding change of temperature is $dT = 0.100$, or if m were altered from 9.931 to 10.050 , T would again be changed only from -7.0° to -6.9° .

We may in a similar manner consider the effect of an error in the reading D on the deduced temperature.

$$\text{For } dD = (m + nT)dT, \text{ or } dT = \frac{1}{m + nT} dD,$$

giving, in the case already considered, $dT = 0.12 dD$, so that an error of a unit on D would only alter the value of T by an eighth of a degree.

These numerical results may be summarised by saying that, in the neighbourhood of the temperature of solid hydrogen under exhaustion, it would require an alteration of $1\frac{1}{2}$ per cent in the values of D or m , and as much as 13 per cent in the value of n , to alter the value of T by one-tenth of a degree.

In general it may be noted that, for an alteration of the same actual (but small) magnitude in the values of n , m , and D respectively, the corresponding alterations of T are proportional to $\frac{1}{2}T^2$, T , and 1.

The general results with the German-silver platinum junction are summarised in Table III., the typical equation being $dE/dt = m + nT$.

TABLE III.

Source of constants.	m .	n .	Melting-point of hydrogen.	Solid hydrogen exhausted.
(3) and (6).	12.52	0.108	16.4°	15.27°
(4) " (6).	11.49	0.158	15.9	14.7
(5) " (6).	9.931	0.231	15.0	13.5
Graphically	10.2	0.167	15.5	14.15
Mean..	—	—	15.7	14.4

For reasons already mentioned, the temperatures deduced from the (5) and (6) set of experiments are in all probability the most accurate in the thermo-electric series of observations.

It is interesting to compare these results with those given in my former paper on the "Boiling-point of Liquid Hydrogen Determined by Hydrogen and Helium Gas Thermometers" (*Proc. Roy. Soc.*, 1901, vol. lxxviii.). Although the main object of that paper was the accurate determination of the boiling-point of hydrogen, I included in the experiments the recorded temperature of solid hydrogen under exhaustion of from 30 to 40 m.m., as given by a hydrogen gas thermometer filled initially at a pressure of 269.8 m.m. at 0°C . This thermometer gave the boiling-point of hydrogen as 19.63° , and the solid under exhaustion as 14.34° ; in other words, the gas thermometer value is just about a mean of the results given by the thermo-junction. This is, so far, confirmatory of the reliability of the thermo-junction as a thermometric agent at the lowest steady temperature we can command.

Although it is not recorded in the paper on the "Boiling-point of Hydrogen," I found that the same helium thermometer which I used for determining the boiling-point gave in exhausted solid hydrogen the temperature of 13.65° , but as the helium had to be corrected for the presence of a small amount of neon, the result might be a little too low. My intention at the time was to defer the consideration of the temperature of solid hydrogen for a further communication to the Royal Society, as distinctly stated in the original paper.

It is true that in a paper on "Solid Hydrogen," read at the British Association in 1899 (*Nature*, September 21, 1899), that is two years before, I gave the approximate melting-point of hydrogen as between 16° and 17° absolute. This value was based on observing the melting-point pressure of solid hydrogen as being about 55 m.m., and therefrom calculating what the temperature should be at this pressure by means of a mean Rankine formula. From the later experiments contained in my paper of 1901 a more accurate Rankine formula can be deduced, viz.,—

$$\log p_H = 6.2874 - 68.02/t,$$

and this gives the approximate temperature of 14.96° as corresponding to 55 m.m., thus bringing the melting-point given by the gas thermometer into substantial agreement with the lowest thermoelectric value.

As a record of the behaviour of the German-silver platinum thermo-junction Table IV. has been calculated from the equations derived from the set of observations (5) and (6), namely:—

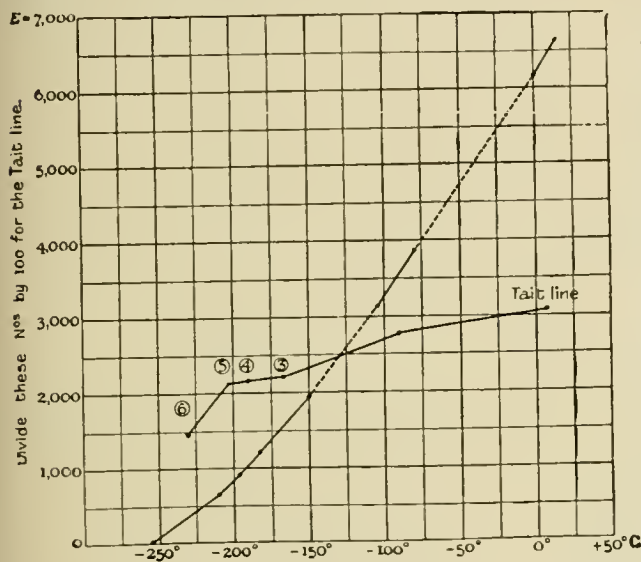


FIG. 2.—THERMO-ELECTRIC JUNCTION.

$$E = \frac{1}{8.64} T (T + 85.8) \text{ and } \frac{dE}{dt} = 9.931 + 0.231 T,$$

when one of the junctions of the couple is assumed to be kept in boiling hydrogen, and the other either falls or rises through a range of some 15° on either side of this temperature, which is about 20.5° absolute. These values show that, at as low a temperature as 6° absolute, the sensibility of this couple is still half what it was at 20.5° absolute, and therefore that, unless some absolute breakdown in the law connecting electromotive force and temperature below 14° takes place, it must continue to be an excellent thermometer, and will record temperature with considerable accuracy down to the boiling-point of helium, which is about 5° or 6° absolute. A further paper will detail the results obtained in the study of the behaviour of helium at low temperatures.

TABLE IV.

t abs.	dE/dt.	E.
35°	13.281	168.32
32°	12.588	129.51
29	11.895	92.77
26	11.202	58.09
23	10.509	25.55
20.5°	9.931	nil
18	9.354	- 24.10
15	8.661	- 51.12
12	7.968	- 76.05
9	7.275	- 98.90
6	6.582	- 119.70

I am indebted to Mr. T. D. H. Dickson, M.A., of St. Peter's College, Cambridge, for help in the discussion of the results, and to Mr. Robert Lennox, F.C.S., for assistance in the conduct of the experiments.

THE WEIGHTS OF OXYGEN, NITROGEN, AND HYDROGEN.

By C. J. T. HANSEN, C.E.

PROFESSOR SIR JAMES DEWAR's excellent experiments on oxygen, nitrogen, and hydrogen, described in a paper read before the Royal Society, March 17, 1904, and published in the *CHEMICAL NEWS* (vol. lxxxix., pp. 205, 217), are of high importance, as in these experiments the liquefied and solidified gases operated upon have, in the process of cooling, been more perfectly purified than is possible by chemical means; and, being contracted to a comparatively very small volume, may be weighed more exactly than by the usual weighing of gas in large glass balloons.

Sir James Dewar might at the same time have settled the important and vexed question of the absolute and the atomic weight of these gases; this, however, has not been his intention. He has taken the weight of 1 litre of gas at 0° C. and 760 m.m. pressure as—

Oxygen	= 1.43 grms.
Nitrogen	= 1.2564 "
Hydrogen	= 0.0899 "

The volume of the condensing flask was—

For O at $+15^\circ$ C. . . .	= 23.9212 c.c.
" N and H at $+14.2^\circ$ C. .	= 22.1454 "

The coefficient of cubical expansion by heat (or contraction by cold) of glass was taken = $0.0000250 = 1/40000$ of volume for 1° C. from $+15^\circ$ C. down to the lowest temperatures.

If the volumes of gas used in the experiments are reduced to uniform temperature, $\pm 0^\circ$ C. = 273° C. abs., and to 760 m.m. pressure, we get—

Table I.	1. Oxygen . .	18610596 cubic m.m.
"	2. " . .	19468555 "
"	4. " . .	23686880 "
Table II.	1. Nitrogen . .	14100550 "
"	3. " . .	17969380 "
Table III.	1. Hydrogen . .	17134642 "
"	3. " . .	18670470 "

The volume of the condensing flask for O, which at $+15^\circ$ C. (= 288° C. abs.) is = 239212 c.c., will, according to the coefficient of contraction adopted in the experiments, be—

Table I.	1. At -182.5° C. (= 90.5° C. abs.)	= 23803.089
"	2. " -195.5° C. (= 77.5° C. abs.)	= 23795.116
"	4. " -252.5° C. (= 20.5° C. abs.)	= 23761.227

The condensing flask for N and H, which at $+14.2^\circ$ C. (= 287.2° C. abs.) is = 22.1454 c.c., is—

Table II.	1. At 195.5° C. (= 77.5° C. abs.)	= 22029.303
" III.	1. " 252.5° C. (= 20.5° C. abs.)	= 21997.746
" III.	3. " 259.9° C. (= 13.1° C. abs.)	= 21993.649

The volume of gas at 273° C. abs. and 760 m.m. pressure, condensed and filling the flask, = $\frac{\text{Volume of gas}}{\text{Volume of flask}} =$
1 volume condensed gas.

TABLE I.—Oxygen.

$^\circ$ C. abs.	Cubic m.m.	Vols. gas.
1. 90.5°	$\frac{18610596}{23803.089}$	= 781.856 = 1 vol. liquid O 90.5°
2. 77.5°	$\frac{19468555}{23795.116}$	= 818.174 = 1 vol. liquid O 77.5°
4. 20.5°	$\frac{23686880}{23761.227}$	= 996.871 = 1 vol. solid O 20.5°

TABLE II.—Nitrogen.

$^\circ$ C. abs.	Cubic m.m.	Vols. gas.
1. 77.5°	$\frac{14100550}{22029.303}$	= 640.077 = 1 vol. liquid N 77.5°
3. 20.5°	$\frac{17969380}{21997.746}$	= 816.874 = 1 vol. solid N 20.5°

TABLE III.—Hydrogen.

$^\circ$ C. abs.	Cubic m.m.	Vols. gas.
1. 20.5°	$\frac{17134642}{21997.746}$	= 778.927 = 1 vol. liquid H = 20.5°
3. 13.1°	$\frac{18670470}{21993.649}$	= 848.903 = 1 vol. solid H = 13.1°

We may conveniently take these volumes = litres. Then, 781.856 litres O gas of 273° C. abs. and 760 m.m. pressure are = 1 litre liquid O of 90.5° C. abs., and multiplying by the adopted weight per litre of gas, we get the specific gravity of the condensed liquid or solid gas as—

TABLE I. Oxygen (273° C. abs.).

C. abs.	Litres.	Grms.	Grms.	C. abs.
90.5°	781.856×1.43	= 1118.05408	= 1 litre liquid O	90.5°
77.5°	818.174×1.43	= 1169.98882	= 1 litre liquid O	77.5°
20.5°	996.871×1.43	= 1425.52553	= 1 litre solid O	20.5°

TABLE II.—Nitrogen.

C. abs.	Litres.	Grms.	Grms.	C. abs.
77.5°	640.077×1.2564	= 804.19274	= 1 litre liquid N	77.5°
20.5°	816.874×1.2564	= 1026.32049	= 1 litre solid N	20.5°

TABLE III.—Hydrogen.

C. abs.	Litres.	Grms.	Grms.	C. abs.
20.5°	778.927×0.0899	= 70.02554	= 1 litre liquid H	20.5°
13.1°	848.903×0.0899	= 76.30538	= 1 litre solid H	13.1°

These values agree very closely with the densities in Professor Dewar's Tables I., II., and III. (column d).

But these densities are correct only if the adopted coefficient of expansion of glass and the weight per litre of O, N, and H gas of 273° C. abs. and 760 m.m. pressure (London latitude) are correct.

That the coefficient of expansion of glass = 1/40000 of the volume down to the lowest temperatures appears to be questionable, although Prof. Dewar has adopted it.

All kinds of glass, fused silica not excepted, expand at +300° C. three to four times more than at +100° C., and at 0° absolute the expansion evidently must be = 0.

The proper scale for cubical expansion of glass by heat (and contraction by cold) to suit the prevailing circumstances must be a curve, which, very nearly correct, may be found thus:—

Suppose the condensing flask at $\pm 0^\circ$ C. (273° C. abs.) contains 1000000 volume-units, it will then expand by heat or contract by cold at the rate $\frac{n^\circ \text{ C. abs.}}{10}$. At absolute 0° (= -273° C.) it will be decreased.

$\frac{273^\circ}{10} = \frac{74529}{10} = 7453$ vol.-units and remain 1000000 - 7453 = 992547 volume-units; at $\pm 0^\circ$ C. (= 273° C. abs.) it is 1000000 volume-units, and—

°C.	°C. abs.	Vol. units.
At +15 (= 288)	$\frac{288^\circ}{10} = 8294$	+ 992547 = 1000841
" +14.7 (= 287.2)	$\frac{287.2^\circ}{10} = 8248$	+ 992547 = 1000795
" 90.5	$\frac{90.5^\circ}{10} = 819$	+ 992547 = 993366
" 77.5	$\frac{77.5^\circ}{10} = 601$	+ 992547 = 993148
" 20.5	$\frac{20.5^\circ}{10} = 42$	+ 992547 = 992589
" 13.1	$\frac{13.1^\circ}{10} = 17$	+ 992547 = 992564
" +300 (= 573)	$\frac{573^\circ}{10} = 32833$	+ 992547 = 1025380

Professor Dewar's condensing flask for oxygen, which at +15° C. (288° C. absolute) has volume 23921 cubic m.m., will, at this rate of contraction,—

At 90.5° C. abs. contain 23742.540 cubic m.m.
" 77.5° " " 23737.330 "
" 20.5° " " 23733.529 "

And the flask for nitrogen and hydrogen, which at +14.2° C. (287.2° C. abs.) contains 22145.4 cubic m.m., will—

At 77.5° C. abs. contain 21976.180 cubic m.m.
" 20.5° " " 21972.662 "
" 13.1° " " 21963.258 "

The weight given for nitrogen gas at 273° C. abs. and 760 m.m. pressure seems too high. 1.2564 grms. per litre, if O is 1.43 would be = 1.405751 atomic weight of N if O is 16; while the International Table of Atomic Weights (1904) only has 14.04 for N, and in R. W. Gray's and other experiments it varies between 13.990, 14.004, and 14.007. (See CHEMICAL NEWS, xc., p. 269; xci., pp. 44, 240, 292).

The volume of gas at 273° C. abs. and 760 m.m. pressure condensed and filling the flask = $\frac{\text{Volume of gas}}{\text{Volume of flask}}$ forming 1 volume liquid or solid gas.

TABLE I.—Oxygen.

°C. abs.	Cubic m.m.	Volumes gas.
1. 90.5	$\frac{18610596}{23742.540}$	= 783.850 form 1 volume liquid.
2. 77.5	$\frac{19468555}{23737.330}$	= 820.024 " " liquid.
4. 20.5	$\frac{23686880}{23733.529}$	= 998.035 " " solid

TABLE II.—Nitrogen.

°C. abs.	Cubic m.m.	Volumes gas.
1. 77.5	$\frac{14100550}{21976.180}$	= 641.629 form 1 volume liquid.
3. 20.5	$\frac{17969380}{21972.662}$	= 817.807 " " solid.

TABLE III.—Hydrogen.

°C. abs.	Cubic m.m.	Volumes gas.
1. 20.5	$\frac{17134642}{21972.662}$	= 779.816 form 1 volume liquid.
3. 13.1	$\frac{18670470}{21963.697}$	= 850.077 " " solid.

We may, as above, take these volumes = litres, and find the density or the weight per litre of liquid and solid O, N, and H by multiplying by the weight per litre of gas of 273° C. abs. and 760 m.m. pressure. If we multiply by Professor Dewar's weights we get—

Oxygen.

°C. abs.	litres.	Grms.
90.5	783.850	$\times 1.43 = 1120.90550 = 1$ litre liquid O.
77.5	820.024	$\times 1.43 = 1172.63432 = 1$ " liquid O.
20.5	998.035	$\times 1.43 = 1427.19005 = 1$ " solid O.

Nitrogen.

77.5	641.629	$\times 1.2564 = 806.14268 = 1$ " liquid N.
20.5	817.807	$\times 1.2564 = 1027.49271 = 1$ " solid N.

Hydrogen.

20.5	779.816	$\times 0.0899 = 70.10546 = 1$ " liquid H.
13.1	850.077	$\times 0.0899 = 76.21922 = 1$ " solid H.

But these weights per litre (O=16) correspond to the atomic weights N=14.575, C=12.007, H=1.0076, &c.—all determined before argon, helium, neon, and other gases which are contained in our atmosphere, in water, and in minerals, were known or suspected to exist, and before gases could be separated and purified by distillation at very low temperatures. With the means now available, chemists and physicists will soon ascertain and remove the last traces of known or still unknown gases which combined with H make it appear heavier than one-sixteenth of O. The atomic weight of C., which a few years ago was taken = 12.007, is now acknowledged to be 12.000 (O=16.00), and so will N soon be = 14 and H = 1.

In the hope that the number of elements whose atomic weights now are expressed by integers may very soon be considerably increased, I multiply the volumes of gases found by the weights per litre,—

Atomic weight.	London latitude.	Latitude 41° 10'.
O = 16	1.42992 grms.	10/7 grms.
N = 14	1.25118 " "	10/8 " "
H = 1	0.08937 " "	5/56 " "

and find the specific gravity and the weight per litre of the condensed gases (London latitude):—

°C. abs.	Litres.	Grms.	Grms.
O. 90.5	783.850	$\times 1.42992 = 1120.84279 = 1$ litre liquid.	
77.5	820.024	$\times 1.42992 = 1172.56872 = 1$ " "	
20.5	998.035	$\times 1.42992 = 1427.11021 = 1$ " solid.	
N. 77.5	641.629	$\times 1.25118 = 802.79337 = 1$ " liquid.	
20.5	817.807	$\times 1.25118 = 1023.22376 = 1$ " solid.	
H. 20.5	779.816	$\times 0.08937 = 69.69216 = 1$ " liquid.	
13.1	850.077	$\times 0.08937 = 75.97138 = 1$ " solid.	

Copenhagen V., Valdemarsgade 3.

THE
DEVELOPMENT OF SPECTRO-CHEMISTRY.*

By Professor JULIUS WILHELM BRÜHL, Ph.D., Sc.D.,
Hon. Mem. R.I., Professor in the University of Heidelberg.

ASSOCIATED as I am with Great Britain in my capacity as a Member of the Royal Institution, it is a special pleasure to me this evening to sketch to you the development of a branch of scientific study, the early history of which was enacted in this country—a country to which for many years I have been bound by close ties of sympathy. Many of you know already, and the others will see this evening, that I am in especial measure indebted to the science of this country for stimulus and encouragement in my own studies. It is a source of deep satisfaction to me to testify here to the gratitude which I owe to British science.

I.

1. Last August it was my privilege to attend the Meeting of the British Association on the classic ground of Cambridge, and one sunny afternoon I found my way into that peculiarly effective example of collegiate architecture, the Chapel of Trinity College. The organ was playing Bach's Passacaglia, and I sat down quietly at the foot of the marble statue which bears the inscription:—

NEWTON.

Qui genus humanum ingenio superavit.

The empty chapel was filled with harmony and with memories of the great man who once had sojourned there. And my thoughts wandered back to the past.

In 1666, almost two and a-half centuries ago, Isaac Newton, then a young bachelor, had decomposed a beam of sunshine, discovered the diverse refrangibility of the coloured rays, and explained the phenomena of dispersion.

The founder of scientific optics was also the first to perceive a connection between differences in the composition of various natural bodies and their power of transmitting light.

Newton observed that oils, amber, sulphur, and other combustible bodies possess great refractive power, and he made the remarkable statement that the diamond must also be combustible, because it refracts light so powerfully. This statement is indeed remarkable when we remember that in those distant times no one had any idea of the chemical composition of the diamond, or any conception of the nature of combustion.

But centuries of patient work were needed in order to recognise clearly the connection between the chemical composition of different bodies and their power of refracting and dispersing light in different ways, *i.e.*, of producing differently constituted spectra. To account for this connection has become the task of "Spectro-chemistry."

2. Newton was also the first to fix a standard for measuring the refractive power of bodies. Starting from the emanation theory of light which he had himself founded, he diminished the square of the refractive index, n , by unity and regarded—

$$n^2 - 1$$

as the expression for the refractive power. This power, reduced to constant density, *i.e.*, divided by the specific gravity d of the body:—

$$\frac{n^2 - 1}{d}$$

was called by Newton the "absolute refractive power."

3. It was fully a hundred years later that Laplace, in his celebrated "Mécanique céleste," laid down the principle that the expression for refraction, derived from Newton's emanation theory, must for one and the same substance be unaffected by changes in density caused by temperature and pressure—unaffected, that is, by the accidental density of a substance.

4. The hitherto purely hypothetical formula for refraction acquired further scientific importance from the researches of Biot and Arago (1806), and Dulong (1826), on the refractive powers of gases and vapours. These, the first quantitative measurements of refractivity, seemed actually to confirm the theory that Newton's formula denotes a constant quantity which always remains unaffected by the accidents of temperature and pressure.

But with the triumph of the modern wave-theory of light, Newton's expression for refraction, $\frac{n^2 - 1}{d}$, lost its theoretical importance. New experiments soon showed that even its supposed independence of temperature and pressure did not in fact exist.

II.

5. In 1858, John Hall Gladstone, who was for some time Professor in this Institution, began his splendid series of optical researches, which he pursued with great success for over forty years. At first in collaboration with the Rev. T. Pelham Dale he investigated the dependence of refractivity on temperature in the case of fluid substances. The important fact was at once established that Newton's expression for refraction $\frac{n^2 - 1}{d}$, is not constant, but varies considerably with the temperature. On the other hand, it was found that the more simple ratio—

$$\frac{n - 1}{d}$$

remains practically constant.

Now this ratio, just like the Newtonian constant confirmed by Biot and Arago, and by Dulong, applies also to gases and vapours. As, in the case of gases, the refractive index is very little different from unity, the numerical value of $\frac{n^2 - 1}{d}$ is almost exactly twice that of $\frac{n - 1}{d}$.

III.

6. Soon after 1860, Hans Landolt came forward with his optical researches. He began by confirming the results of Gladstone and Dale. He proceeded a step further, however, by following the example of Berthelot, and comparing the refractivity not of equal, but of molecular quantities of the substances. If P represents the molecular weight, the product $\left(\frac{n - 1}{d}\right) P$ is the molecular refraction.

7. Landolt examined particularly the fundamental question whether a different grouping of the same number of atoms of the same elements—which is the cause of isomerism—has any influence on the optical properties of bodies.

He established the important fact that only the relative weight of the elements is of influence on the molecular refraction of a compound, while the different grouping of the atoms has no appreciable effect; and this made it possible to determine the atomic refractions of the elements. The atomic refraction of carbon, for instance, was obtained by comparing the molecular refractions of two compounds which differed only by one atom of carbon; and in a similar manner the atomic refractions of the remaining elements were determined.

With the aid of these constants it was now possible to calculate *a priori* the molecular refraction of many organic compounds from the elements composing them, and Landolt showed that the calculated molecular refractions agreed very well with those determined by experiment.

8. Gladstone, in the course of his researches, was able to confirm Landolt's results in many cases. But he also found a considerable number of substances in which the observed molecular refraction was completely at variance with that obtained by adding the atomic refractions together. The exceptions were so numerous, that they really seemed to overthrow the whole law of summation.

IV.

9. Shortly before 1880, when I was studying the literature of chemical optics, a brief note published by Gladstone in

* A Lecture delivered at the Royal Institution, May 26, 1905.

the *Journal of the Chemical Society* for May, 1870, excited my attention and curiosity. The author there discusses the exceptions to Landolt's rule of summation. He shows firstly that in all such cases the molecular refraction is never found to be too small, but always too great. Then he shows that whole classes of compounds behave in this abnormal fashion.

10. All optically abnormal compounds proved to be rich in carbon. Gladstone therefore examined the effect which a gradual increase of carbon in the composition of a body exerted on its refractivity. He found that there actually was an increase in the excess of the experimental as compared with the calculated molecular refraction, but the increase was not regular enough to explain the anomalies.

The saturated hydrocarbons or *paraffins*, of the general composition C_nH_{2n+2} , showed *normal* molecular refraction.

Also the *olefines*, containing two atoms less of hydrogen, were found normal by Gladstone.

On the other hand, the hydrocarbons containing six atoms less of hydrogen, viz., the *terpenes*, gave molecular refractions about 3 units larger than would correspond to their composition.

With the aromatic hydrocarbons, such as benzene, toluene, &c., containing eight atoms less of hydrogen, this abnormal excess amounted to 6 units:—

Paraffins	(C_nH_{2n+2})	Normal
Olefines	" $-H_2$	"
Terpenes	" $-H_6$	" +3
Benzene and derivatives ..	" $-H_8$	" +6

With still further decrease in the quantity of hydrogen contained (*i.e.*, with further increase of carbon), there resulted greater and greater refractive increments.

The last member of the series, however—pure carbon without any hydrogen, represented by the diamond—proved to be perfectly normal in its optical properties.

V.

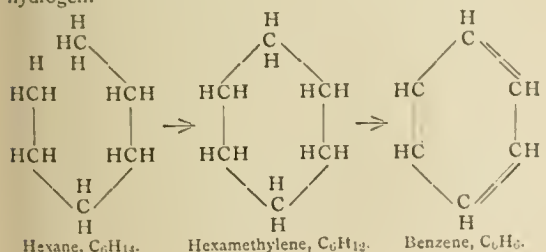
11. François Arago, when sketching in his celebrated "Eloges" the life and work of Thomas Young, relates that the latter was led to his fundamental discovery of the interference of light by nothing more extraordinary than soap-bubbles. In this connection Arago remarks that it is one of the most precious gifts to be able to wonder at the right time.

Gladstone's observations just mentioned had been known almost ten years without anybody's surprise being excited. When his short note came into my hands, I was fortunate enough to begin wondering at the right time.

It seemed to me really extraordinarily remarkable that all optically abnormal substances, without exception, gave a too *high* molecular refraction. It was no less astonishing to me that the saturated hydrocarbons were optically normal, but became more and more abnormal at successive withdrawals of hydrogen—while pure carbon, uncombined with hydrogen, is again completely normal.

But I was most particularly struck by the quantitative amount of the abnormality in the case of benzene compounds, especially their refractive increment of six units. The number 6 fascinated me. I could not help thinking that therein lay the key to the mystery, and I lost no time in making use of it.

12. According to Kekulé's ingenious hypothesis we can imagine benzene, C_6H_6 , to have arisen from the saturated hydrocarbon hexane, C_6H_{14} , by successive removal of hydrogen.



Thus altogether four pairs of hydrogen atoms have been removed. The elimination of the first pair was made the occasion to form another *simple* carbon bond like those already present in hexane, and with it the ring was closed. The splitting-off of the other three pairs of hydrogen atoms, on the other hand, resulted in the formation of three *double* bonds of carbon atoms—a kind of bond which does not occur in the optically normal hexane.

Now Gladstone had found that benzene exhibits a refractive increment of 6 units. Reading this I was struck in a moment by the thought:—Might not this abnormal refractive increment of benzene be due to its double carbon bonds, which are absent in the optically normal hexane?

And if this were so, I went on to reason, since *three* double bonds in benzene correspond to a refractive increment of 6 units, therefore *one* double bond must entail the increment of 2.

These ideas received no support whatever from the then known facts. For Gladstone had stated expressly that the olefines, *i.e.*, open-chain hydrocarbons, containing one double carbon bond, were optically *normal*.

However, I did not allow myself to be discouraged; and, behold! my expectations were confirmed by the very first experiment. The olefine examined not only proved to be optically abnormal, but gave the predicted refractive increment of 2 units, corresponding to the presence of *one* double carbon bond.

Gladstone, therefore, as I had supposed, was mistaken in this case. Further experiments proved that not one of the olefines was optically normal. Without exception they gave the refractive increment of 2 units, one-third of that of benzene.

I next proceeded to examine the diolefines—substances which contain *two* double carbon bonds. Here also, in conformity with expectation, a constant refractive increment was found, double as large as that of the olefines and two-thirds of that of benzene:—

Paraffins	(C_nH_{2n+2})	Normal
Olefines	" $-H_2$	" +2
Diolefines	" $-H_4$	" +4
Benzene compounds ..	" $-H_8$	" +6

The dimensions of our subject this evening prevent the detailed demonstration of these important facts by experiment. I will only show you that the spectrum of a saturated hydrocarbon (a paraffin) is distinguishable at a glance from that of a substance containing double bonds.

On this screen we project the electric spectrum of metallic calcium. First we cause the rays of light to pass through a prism filled with paraffin-oil. Then we exchange this prism for another, filled with a substance containing atoms linked by double bonds. (Experiment.)

In the second case you observe, firstly, a much greater deviation of the whole spectrum, *i.e.*, greater *refraction*, and, secondly, far wider intervals between the coloured lines of the spectrum, *i.e.*, greater *dispersion*, which is usually correlative to the refraction.

13. Thus quantitative experimental confirmation was obtained for the view that abnormal refractive increments which increase with the diminution of hydrogen contained in the substances, are caused by the presence of double carbon bonds.

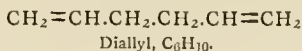
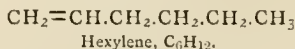
At the same time, however, the experiments yielded a second result of fundamental importance. The olefines contain 2, and the diolefines 4 atoms of hydrogen less than the paraffins. Similarly the refractive increment of the olefines is 2, and of the diolefines 4.

Benzene, C_6H_6 , contains 8 atoms of hydrogen less than the corresponding paraffin, hexane, C_6H_{14} . The increment of benzene, however, amounts not to 8, but to 6! Thus in the formation of benzene from hexane, 2 atoms of hydrogen have been eliminated without influence on the refractive increment of the product.

But in the formation of benzene from hexane, 2 atoms of hydrogen have been employed to close the ring (see diagram, at Section 12). The withdrawal of these two atoms and

the closing of the ring have therefore taken place without causing any optical anomaly.

In the formation of the olefines and diolefines from the paraffins, however, there is no closing of the ring. These substances are of open-chain structure, and every removal of 2 hydrogen atoms corresponds here to the creation of a double carbon bond :—



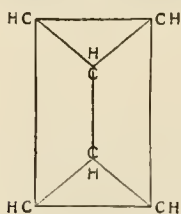
Hence, also, the refractive increment of the olefines and diolefines is directly proportional to the number of hydrogen atoms removed from the paraffin.

From all this it follows that the removal of hydrogen atoms causes optical anomalies only where double carbon bonds are created by the process. *The splitting-off of hydrogen which results in the closing of a ring is, on the other hand, without abnormal optical influence, and produces no refractive increment.*

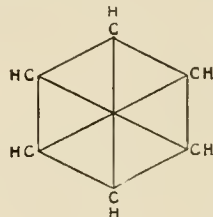
This latter principle, which has since been confirmed many times by experiment, has proved of the same importance as the first in the investigation of the chemical structure of bodies.

14. A few examples will show how these two principles can be utilised for the discovery of chemical structure.

Besides the formula already mentioned for benzene—that suggested by Kekulé—several others have been proposed, e.g., those by Ladenburg and Claus :—



Ladenburg.



Claus.

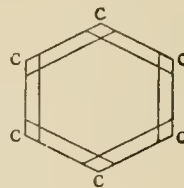
Neither of these graphic formulæ is reconcilable with the results of spectro-chemical investigation, because the neighbouring carbon atoms contained in them are associated only by single cycloid or ring-closing affinities, and not by any so-called double bonds. Substances of this kind should be optically normal, while benzene and its derivatives are, as a matter of fact abnormal. Kekulé's formula for benzene is really the only graphic representation of its structure in a single plane which is confirmed by chemical optics.

Thus it can be at once determined by optical methods whether a given body belongs to the paraffinoid, olefinoid, or cycloid products ; whether these products contain double bonds or not ; and if so, how many.

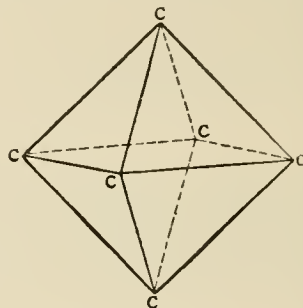
Now, too, we can imagine why the diamond, i.e., pure crystallised carbon, is, as already mentioned, optically normal. We obtain an idea of the mineral's chemical constitution, and of the way in which the atoms of carbon are perhaps combined in the sparkling gem.

For the reasons already stated, the diamond cannot possibly contain any double bonds ; a combination, say, in the form shown in the figure (see top of next column), with one atom of carbon at each of the six corners, and with each atom connected with its neighbour by a double bond, is altogether impossible.

Imagine, however, at each of the six corners of a regular octahedron, a single molecule of marsh-gas, CH_4 , i.e.,



altogether C_6H_{24} , and then imagine all the 24 hydrogen atoms successively removed, so that each carbon atom is connected with each of its neighbours only by a single bond, and thus all six atoms of carbon are united together in a single whole. Then you obtain, as the most simple representation of the molecule of the diamond, a regular octahedron, with one atom of carbon at each of its six corners, while the edges represent the mutual bonds :—



Several simple molecules of this kind may be combined into one crystallised particle of the spectrochemically normal diamond.

15. Thanks to the explanation of the optical behaviour of benzene, with the resultant discoveries, it all at once became possible to understand the causes of the spectro-chemical abnormality of whole classes of bodies, such as the olefines, diolefines, terpenes, aromatic compounds, &c., and light was cast on the chemical constitution of whole classes of bodies.

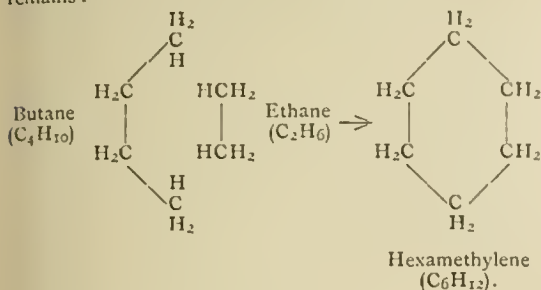
At the same time, however, it at once became apparent why both Landolt and Gladstone had succeeded in observing complete optical normality in very numerous substances of the most various types—alcohols, acids, ethers, hydrocarbons, &c. And now it was understood why in such bodies the molecular refraction is determined solely by the component elements, while the different grouping of the atoms, i.e., the isomerism, remains without any appreciable optical influence.

All the bodies of this kind proved to be either paraffins, i.e., saturated hydrocarbons or simple derivatives of the same. But the paraffins, as we now know, are always optically normal, because they contain no double carbon bonds. For this reason all such simple derivatives of the paraffins must also be normal. Their molecular refraction will thus always correspond to the elements of which they are composed, however the atoms may be grouped, i.e., chemical isomerism is here also without influence.

16. For the same reason, however, all cycloid (ring-shaped) closed formations, if they contain no double carbon bonds, must be optically normal, for those bodies also may be conceived as originating in the simple replacement of hydrogen by paraffin fragments, and may therefore be regarded as combined paraffins.

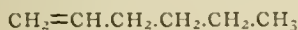
Thus we can imagine the hexamethylene already mentioned not only as formed from hexane by removal of two hydrogen atoms from the ends, but also as arising from ethane and butane, i.e., from two paraffins, by the removal

of four hydrogen atoms and welding together of the remains :—



As a combined paraffin, hexamethylene must be normal, as is also confirmed by experiment, and here we see again, as in the case of the diamond, that a progressive removal of hydrogen and increase of carbon need not lead to the slightest optical anomaly.

At the same time there arises here a case of the optical influence of isomerism, for hexylene, which has already been mentioned, with the same formula (C_6H_{12}) as hexamethylene, but in structure an olefine :—



possesses the familiar refractive increment of 2 units. This example again shows how the spectro-chemical behaviour of a body discloses its chemical structure by enabling us to distinguish with certainty between an optically normal cycloid (or ring-substance), and an isomeric open-chain olefinoid formation, which is optically abnormal.

(To be continued).

THE ISOLATION OF TERBIUM.

By G. URBAIN.

In a previous paper (*Comptes Rendus*, vol. cxxxix., p. 736) I stated that I had just obtained an earth which in solution showed a visible single absorption band, $\lambda = 488$, characteristic of an element which M. Lecoq de Boisbaudran called by the notation $Z\delta$. This earth, which is immediately connected with gadolinium in the series of these rare earths, can be obtained by three distinct methods of fractionation :—(a) Crystallisation of the double nitrates of this earth and nickel, (b) crystallisation of simple nitrates in presence of bismuth nitrate, (c) crystallisation of the ethyl sulphates.

Besides the characteristics of $Z\delta$ this earth shows the fluorescence spectrum (inverse spectrum), which M. Lecoq de Boisbaudran attributes to an element, $Z\beta$ (*Comptes Rendus*, vol. c., p. 1437; 1883, vol. ci., pp. 552, 558; 1886, vol. cii., p. 899), the spark spectrum which Demarcay attributes to an element, Γ (*Comptes Rendus*, 1900, vol. cxxxi., 387), and the phosphorescence spectrum which Sir W. Crookes has attributed both to a meta-element of yttrium and to an element G.3.

This earth, however, also contains gadolinium. To completely separate the pure earth from gadolinia, I first fractionated the double nitrate of this earth and nickel; after this, to eliminate the last traces, I further fractionated, on M. Lecoq de Boisbaudran's advice, by means of ammonia, which concentrated the most basic portions in the tail of the fractionation.

I thus obtained about 7 grms. of an earth which, after incessant fractionations for nearly a year, I found to be identical with the experimental definition of the element.

The principal characteristics of this earth, to which the name of terbium may be strictly reserved, are as follows :—

Absorption Spectrum of Neutral Chloride Solution.

λ .	
488	The middle point of a diffused band, $Z\delta$, one of the least intense of this spectrum.
382.5—374.9	Diffused band. Faint from 382—379; stronger from 379—375.
371.0—367.7	Diffused band; relatively strong.
361—357.2	Medium; diffused.
354.2—349.6	Diffused double band. Between 354.2 and 352 of mean intensity; from 351.7—349.6 more intense.
343—341	Medium diffused.
340—338.4	" "
328.8—324.3	Intense band; very wide and very diffused. The maximum intensity is at 326.
319.2—315.9	Intense, much diffused band.
304.5—301.2	Approximate limits of a generally indistinct band.

The general intensity of this spectrum is faint compared with that of the spectrum of dysprosium, which I intend to describe shortly. The general faintness of the spectrum caused me to doubt for some time the homogeneity of the earth.

The chloride solution gives a reversed, very bright spark, and a beautiful green fluorescence ($Z\beta$ of M. Lecoq de Boisbaudran).

The pure oxides do not give any visible phosphorescence. The oxide of teriferous gadolinium gives a green phosphorescence ($G\beta$ of Sir W. Crookes). A trace of terbium diluted with a considerable mass of alumina gives a magnificent white phosphorescence almost identical with that of a specimen (formed of $Z\delta_2O_3 \cdot 5Al_2O_3$), which M. Lecoq de Boisbaudran kindly lent me. This reaction is of a remarkable sensibility.

The line spectrum will be described later.

It contains more than a thousand lines, of which the greater number are faint and often diffused. The eight strongest have been described by Demarcay under the notation Γ .

All these characteristics diminish simultaneously both as the gadolinium and dysprosium ends of the fractionation are approached. The colour of the oxide varies with the conditions of the preparation. The oxalate, when calcined in a muffle furnace, gives an extremely dark brown oxide, whilst the sulphate calcined at 1600° gives a black oxide.

Terbium oxide, when calcined at a high temperature, is unattacked by cold hydrochloric and nitric acids. The action of dilute acids is also very slow even when hot; intermediate colloidal oxides being produced analogous to those which M.M. Wyruboff and Verneuil have described for cerium under the name of condensed oxides. Solutions of pure terbium are colourless, and the salts are analogous to those of gadolinium, but are in general a little more soluble.

Terbium sesquioxide is white and not pyrophoric.

The determination of the atomic weight has been effected by the estimation of the water in the hydrated sulphate. M. Wyruboff, who examined a specimen of this salt, found that the crystalline form is the same as that of the octohydrated sulphates of the earths of this series. Taking $O = 16$, the atomic weight of terbium cannot differ sensibly from 159.2.

Dysprosiferic-terbias, however, have atomic weights often greater than 160.

The proportion of oxygen in the peroxidation has been determined either by reducing the peroxide by means of hydrogen at a red heat or volumetrically by means of iodine solution. The numbers obtained are not constant. They vary between 1.90 and 2.26 per cent of oxygen. The best formula which I have been able to attribute to terbium peroxide is Tb_4O_7 which therefore requires 2.13 per cent of oxygen.

The terbium extracted from xenotime is identical with the terbium extracted from monazite sands. An examination of the arc spectrum by E. Eberhard confirmed these

results. The complete work of this spectroscopist gives a minute description of the yet unknown spectrum of terbium, which element after sixty years has now taken its place among the list of definite elements.—*Comptes Rendus*, cxli., No. 12.

NOTICES OF BOOKS

Smoke Abatement. By WILLIAM NICHOLSON. London: Charles Griffin and Company, Ltd. 1905.

A CONTRIBUTION to the literature dealing with the abatement of the smoke nuisance will always be welcomed, and this particular work contains many useful suggestions. A historical account of the growth of the smoke abatement movement and of the legislation regarding smoke prevention, both in England and abroad, prefaces the discussion of the causes of the nuisance and the various means which have been adopted to do away with it. While the size of the book precludes the possibility of all types of boilers in use being described in it, a useful summary is given of various smoke preventers and fuel savers, and manufacturers and engineers will no doubt gather some useful information from it. The author also discusses the question of stoking, and insists upon the importance of the employment of efficient stokers, whose sole work is firing; it is interesting to notice with regard to the construction of chimneys that the author advocates very decidedly the building of one tall chimney into the flue of which the flues of all the furnaces of the factory lead, although this is a question upon which expert opinion is somewhat divided.

first introducing a set of preliminary questions on each division of the subject, which the student is to answer from his general knowledge. Then a set of experiments is described, illustrating these questions, while at the end of each chapter another and more advanced set of questions is given, together with a few additional problems. The preliminary questions we should imagine would best be answered orally, and in the hands of a good teacher they should be very useful in bringing out the beginners' ideas. The descriptions of the experimental work appear excellent, the directions being quite explicit enough to ensure no mistakes of manipulation being made. The book can be thoroughly recommended, and will no doubt be appreciated highly by teachers of experimental science.

Introduction to Chemical Analysis. By HUGH C. H. CANDY, B.A., B.Sc., F.I.C. London: J. and A. Churchill. 1905.

IN this work the value of quantitative analysis as mental training is recognised, and the enumeration and description of individual tests are subordinated to general discussions of tables and systems and the principles underlying them. As a result the student who works through the book should acquire a valuable habit of mind, and considerable insight into the reasons for the application of the various tests, while at the same time he will do enough analytical work to prepare him for the Preliminary Scientific Examination of the University of London, or the First Examination of the Conjoint Board. Methods of purifying and preparing substances in the pure state, as well as gravimetric and volumetric analysis, are included; the treatment of quantitative work being, however, very brief, and only useful as an introduction to the study of larger works. The book has many characteristic features which mark it out from similar works, and are all in its favour.

An Introduction to the Study of Colour Phenomena. By JOSEPH W. LOVIBOND. London: E. and F. N. Spon, Ltd. New York: Spon and Chamberlain. 1905.

IN this work the author elaborates a new colour theory, to which was awarded a silver medal by the International Jury of Awards at the St. Louis Exhibition in 1904. A new system of colour nomenclature is also introduced, which seems likely to meet all requirements, and the explanations of the theory are illustrated by coloured charts. The author's theory is formulated in a code of nine laws governing visual colour phenomena, and is briefly compared with older theories, an account of its application to scientific and industrial investigations being also given.

A Text-book of Chemical Arithmetic. By HORACE L. WELLS, M.A. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1905.

THIS book contains clear explanations of the usual arithmetical problems which the chemist has to solve in order to interpret his results obtained experimentally, an introduction being devoted to methods of approximate multiplication and division, and to the theory of errors, absolute and proportional. A very good collection of problems and examples is given, some of them requiring considerable dexterity for their solution, while others will be within the powers of the less advanced students. These examples appear to have been judiciously selected and to be typical, while the explanations in the text are such as the student of quantitative analysis should be able to understand readily without additional aid. Tables of five figure logarithms are added.

An Elementary Text-book of Inorganic Chemistry By R. LLOYD WHITELEY, F.I.C., F.C.S. London: Methuen and Co. 1905.

THE author of this work has to a certain extent hampered himself by writing up to a syllabus (that of the Board of Education), but at the same time the book has a definite value of its own, quite apart from examination considerations, and it will be found very serviceable for use in schools. The order in which the facts are put before the reader is thoroughly logical, and in some respects suggests the "heuristic" method; thus after introductory chapters on chemical physics, the study of the air is taken up, with special attention to the phenomena of combustion and rusting; then water and its properties are considered, and a section is devoted to the study of common salt and the chlorides. The chapters on chemical theory are introduced relatively late in the book, while full directions, well illustrated by diagrams, are given for the performance of the numerous experiments described. The book contains a large amount of information, judiciously selected and well arranged, and the large collection of questions at the end will be valuable to teachers.

Select Methods in Food Analysis. By HENRY LEFFMANN, A.M., M.D., Ph.D., and WILLIAM BEAM, A.M., M.D., F.I.C. Second Edition. London: Rebmán, Ltd. 1905.

THE first edition of this book was accorded a very hearty welcome, and the second edition will be found if anything even more valuable. It contains a good deal of new matter, especially as regards the discussion of polarimetry, new processes for the detection of natural colours used as substitutes for fruit and egg colours, &c. Some paragraphs have been omitted to make room for this new matter, but the general plan of the book remains unaltered, and it excellently fulfils its aim of assisting the analyst in his search for adulterations.

Elementary Chemistry. Part I. By F. R. L. WILSON, M.A., and G. W. HEDLEY, M.A. Oxford: Clarendon Press. 1905.

THE first volume of this work contains a very carefully graduated course of mensuration and elementary physics, forming an excellent introduction to the study of chemistry. The subject is attacked entirely from the experimental point of view, and the authors have adopted the plan of

Elektrolytische Verzinkung. ("Electrolytic Zinc Plating").
By **SHERARD COWPER-COLES.** Halle-a-S.: Wilhelm Knapp. 1905.

THE recent developments in the practice of zinc plating are of sufficient importance to warrant the production of a monograph on the subject, such as this small book, which gives a useful summary of modern improvements in the process which is the basis of all methods of zinc plating. Special attention is paid to the mechanical details, in which respect great strides have been made lately, although much still remains to be done, and there is ample scope for the suggestion of improvements. The preparation of the surface of the substance to be covered with zinc, which has to be very carefully performed, is fully described, and altogether the monograph, which has been translated into German by Dr. Emil Abel, gives a very complete account of this branch of electro-plating.

MISCELLANEOUS.

Preparation of Pure Binoxide of Cerium. Its Reduction by Hydrogen.—**R. J. Meyer.**—The materials used by the author for his experiments were cerite and (more especially) the monazite sands. For the purpose of purification, the material was transformed into the double nitrate of ammonium and cerium. To free this salt from the small quantities of thorium which might be present, the solution of the double salt was treated with sulphuretted hydrogen, and then with H_2O_2 at 60–70°. The thorium is precipitated and the cerium remains in solution. From this solution it is precipitated in the form of basic acetate according to the method described by R. J. Meyer and Koss (*Berichte*, xxxv., 676). The basic acetate obtained is transformed again into the double nitrate, and this latter purified by crystallisation in nitric acid. By this process it is possible to obtain a binoxide of cerium which is not absolutely white, but very slightly yellow. However, the compound obtained is not chemically pure, for, by the action of sulphuric acid, it gives a white sulphate of cerium, from which may be isolated a compound giving a reddish oxide. The impurity consists apparently of praseodymium and lanthanum. The praseodymium is separated by fractional crystallisation of the sulphates, and accumulates in the end fractions. The lanthanum is eliminated by Drossbach's method (German Patent No. 143,106), which consists of treating the neutral solution of cerium with permanganate of potassium and carbonate of soda until there is a persistent rose colouration; acidulate then with nitric acid, and filter. The precipitate contains the hydrated binoxides of cerium and manganese. It is decomposed by $(CO_2H)_2 + HCl$. The oxalate of cerium remains insoluble, and by calcination gives an oxide absolutely free from lanthanum. The small quantity of manganese which may be retained is eliminated by washing with sulphurous acid and hydrochloric acid. The strong colouration taken by oxide of cerium under the action of heat, whether this operation is carried out in a platinum or porcelain crucible, should be apparently attributed to molecular condensations. Even at a high temperature the oxide does not lose oxygen. The reduction of the binoxide by hydrogen only takes place in the complete absence of air. The loss of oxygen is from 2.31 per cent at a dull red heat, to 2.62 per cent at a bright red, and 2.76 per cent at a yellow heat. The blue-black oxide thus obtained is very oxidisable, and is rapidly transformed in the air into a yellow mass of binoxide. By repeating this reduction and oxidation several times, it is observed that the binoxide formed has a tendency to lose less and less oxygen under the action of heat. Although the composition of the oxide of cerium resulting from the reduction of the binoxide is not yet known exactly, it is quite certain that it does not correspond to the formula of a sesquioxide. —*Zeit. Anorg. Chem.*, xxxvii., pp. 378–393.

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VOL. XCII., No. 2395.

STUDIES WITH THE LIQUID HYDROGEN AND AIR CALORIMETERS.*

By Sir JAMES DEWAR, M.A., LL.D., Sc.D., F.R.S., Professor of Chemistry at the Royal Institution, and Jacksonian Professor, University of Cambridge.

I. Specific Heats.

THE calorimeter employed in the following researches was similar to that described in my paper on "The Scientific Uses of Liquid Air" (*Proc. Roy. Inst.*, 1894, vol. xiv., p. 398), and in an improved form in Madame Curie's work "Recherches sur les Substances Radio-actives," Second Edition, p. 100. A sketch of the apparatus appears in my paper on "The Absorption and Thermal Evolution of Gases Occluded in Charcoal at Low Temperatures" (*Proc. Roy. Soc.*, 1904, vol. lxxiv., p. 123).

The arrangement employed consists essentially of a large vacuum vessel capable of holding 2 or 3 litres, into which is inserted a smaller vacuum vessel of 25 to 50 c.c. capacity constituting the calorimeter, the latter being sealed on to a long narrow tube which projects from the mouth of the exterior vessel, in which it is lightly held by a loose packing of cotton-wool. A little below the upper end a branch tube is taken off which conveys the volatilised gas from the calorimeter to the gas receiver. To the extremity of the projecting tube a small test-tube, to hold the portions of substance experimented on, is attached by a short piece of rather wide rubber tubing which forms naturally a movable joint that can be bent into any position. With care I have found this valve gives as good results as more elaborate means of securing the dropping of the substances into the calorimeter. A small vacuum vessel containing solid carbonic acid, liquid ethylene, liquid air, &c., into which the test-tube is placed, cools the materials to different temperatures below those of the laboratory, or alternatively it may be heated in the vapour of water or other liquids.

The general constants for liquid gas calorimeters are given in Table I.

Thus an instrument in which liquid air is used has twice the sensibility of a corresponding one in which liquid ethylene is employed, whereas the substitution of liquid hydrogen for liquid air increases the delicacy of the calorimeter some seven times. It is easy to detect the transference of 1/50 of a gramme calorie in the liquid air instrument, whilst 1/300 of a gramme calorie can be similarly observed in the liquid hydrogen form of the calorimeter.

In preparing for use a liquid air calorimeter, some 2 litres of old liquid air containing a high percentage of oxygen are poured into the large vacuum vessel, and the calorimeter, filled with some of the same fluid, is immersed therein. An experiment is conducted by tilting up the little test-tube previously cooled or heated, thereby dropping into the calorimeter a portion of any substance previously weighed. The substance, if left under normal conditions, in this

way falls from the temperature of the room to that of liquid air. The heat given up by it to the liquid air volatilises some of it, which is carried off by the branch tube and measured in a graduated receiver. Immediately preceding or following this observation, a similar experiment is made with a small portion of a selected standard substance, namely, lead. The quantity of lead is so chosen as to produce about the same volume of gas in the receiver as that supplied by the portion of substance experimented on. By this means, the circumstances of the two observations are made as similar as possible, and thereby many sources of error are eliminated.

The handling of the instrument has been carefully studied and improved since the earlier experiments. I find that the vacuum of the calorimeter itself should be a mercury vacuum. Before inserting the calorimeter into the vessel of liquid air, it should have a good deposit of mercury over its surface, obtained by placing a little liquid air in the interior of the calorimeter and allowing it to stand for some time. After a considerable quantity of the liquid air in the calorimeter has been volatilised, the boiling-point of the remaining portion rises slightly above that of the exterior mass of liquid air, and the liquid over which the volatilised gas is collected is apt to "suck back." When this takes place the calorimeter should be emptied and filled anew from the external vessel. The tube coming from the calorimeter ought to be of the size of wide quill tubing, and the free end of the branch tube should be so arranged below the surface of the liquid in the collecting vessel as to produce no resultant pressure. With these precautions it is easy to get results accurate to within 2 per cent.

The use of pure oxygen has no advantage over that of liquid air which has stood for some days, and thus contains a high percentage of oxygen. Pure nitrogen cannot be used without taking special precautions to prevent the atmosphere from getting access to the calorimeter, as otherwise the air liquefies and causes great uncertainty in the working of the instrument.

When liquid hydrogen is similarly used, precautions have to be taken to keep air from getting condensed to the solid state in the neck of the calorimeter. For this purpose, a slow current of dry hydrogen, from an ordinary Kipp apparatus, is kept discharging, partly through the aperture by means of which the bodies fall into the calorimeter, and partly through the tube by which the evaporated hydrogen escapes to the receiver, until everything is ready to make the experiment. The hydrogen is led in by means of a T-shaped piece of tubing, with a stopcock attached, placed between the calorimeter and the gas-collecting receiver.

When the body has to be transferred from solid carbonic acid or liquid air to the calorimeter, the following procedure is adopted:—It is placed in the small test-tube, above the indiarubber joint, which is inserted into a small vacuum vessel containing some of the substance (solid carbonic acid or liquid air), so that at the moment of making the experiment the solid, by a quick vertical movement of the vacuum vessel, is thrown into the calorimeter. A little cotton-wool inserted in the mouth of the vacuum vessel prevents the carbonic acid paste, or liquid air, from being ejected.

Among the sources of error which may occur, the following should be noticed and allowed for. In dropping a small body from the temperature of the laboratory (say)

TABLE I.

Liquid gases.	Boiling-point.	Liquid volume, 1 grm. at boiling-point, in c.c.	Latent heat, in grm.-calories.	Volume of gas at 0° and 760 m.m. per grm.-calorie, in cubic centimetres.
Sulphurous acid	+10°0'	0·7	97·0	3·6
Carbonic acid	-78°0	0·65 (solid)	142·4	3·6
Ethylene	-103°0	1·7 "	119·0	7·0
Oxygen	-182·5	0·9 "	53°0	13·2
Nitrogen	-195·6	1·3 "	50°0	15·9
Hydrogen	-252·5	14·3 "	125°0	88·9

* A Paper read before the Royal Society, June 8, 1905.

TABLE II.

	Number of experiments.	Range of temperature.	Weight, in grms.	Volume of gas in c.c.	Specific heat.
Diamond	4	18° to liquid air	1.901	271.5	$S. H. = \frac{1.164}{1.901} \times \frac{271.5}{106} \times 0.0295 = 0.0463.$
Lead	2		1.164	106.0	
Diamond	2	Solid carbonic to liquid air	1.729	54.0	$S. H. = \frac{0.50}{1.729} \times \frac{54}{23.5} \times 0.029 = 0.0193.$
Lead	1		0.500	23.5	
Diamond	3	Liquid hydrogen to liquid air	2.142	58.5	$S. H. = \frac{1.996}{2.142} \times \frac{58.5}{351} \times 0.0280 = 0.00435.$
Lead	4		1.996	351.0	

TABLE III.—Specific Heats.

Substance.	Number of expts.	Range.	Specific heat.
Diamond	17	Liquid air to 18°	0.04727
	8	Liquid air to solid carbonic acid	0.01905
	3	Liquid hydrogen to liquid air	0.00435
Graphite	1	Liquid air to 19.5°	0.0948
	2	Liquid air to solid carbonic acid	0.0599
	2	Liquid hydrogen to liquid air	0.0133
Ice	3	Liquid air to -18°	0.348
	8	Liquid air to solid carbonic acid	0.285
	2	Liquid hydrogen to liquid oxygen	0.146

TABLE IV.

Substance.	18° to -78°.	-78° to -188°.	-188° to -252.5°.
Diamond	0.0794	0.0190	0.0043
Graphite	0.1341	0.0599	0.0133
Ice	0.463*	0.285	0.146

* This is from -18° to -78°.

TABLE V.

Substance.	Range.	Specific heat.
Diamond	-79.7° to +21.4°	0.0806
Graphite	-79.3° to +21.6°	0.1301

TABLE VI.

Number of observations.	Substance.	Weight used, in grms.	Range of temperature, °C.	Volume of gas, in c.c.	Specific heat.
1	German silver	0.22	-18 to -188	48	0.080
1	Brass	0.627	+19.5 -188	166	0.099
1	Brass	0.244	-188 -252.5	66 (H)	0.043
2	Tellurium	0.645	+18.2 -188	99.5	0.047
2	Sulphur	0.289	+18.2 -188	131	0.137
2	Selenium	0.353	+18.2 -188	80	0.068
2	Potassium alum	0.180	+18.8 -188	152.5	0.256
2	Potassium alum	0.376	-78 -188	130	0.223
2	Chromium alum	0.20	+20 -188	162	0.243
2	Chromium alum	0.392	-78 -188	135	0.222
1	Calcium chloride (hydrate)	0.184	+20 -188	180	0.294
1	Calcium chloride (hydrate)	0.336	-78 -188	141	0.271
3	Sodium chloride	0.105	+16 -188	55.2	0.187
2	Sodium chloride	0.253	-78 -188	65.5	0.164
3	Ammonium chloride	0.054	+16 -188	45.8	0.300
2	Ammonium chloride	0.130	-78 -188	42.5	0.207
2	Naphthaline	0.55	+16 -188	31.5	0.202
2	Naphthaline	0.105	+16 -188	57.25	0.194
1	Naphthaline	0.090	+15 -188	50.5	0.204
2	Naphthaline	0.203	-78 -188	40.6	0.126
1	Paraffin	0.08	+15 -188	68.5	0.312
1	Paraffin	0.105	-78 -188	38.5	0.176
1	Silver iodide	0.307	+16 -188	44.5	0.052
2	Silver bromide	0.196	+16 -188	35.5	0.064
2	Silver chloride	0.215	+16 -188	49.75	0.082
5	Solid carbonic acid	0.164	-78 -188	57.1	0.215
1	Solid carbonic acid	0.15	-78 -182.5	50	0.225
1	Solid carbonic acid	0.190	-78 -182.5	62	0.223
2	Solid ammonia	0.14	-103 -188	72.25	0.519
2	Solid ammonia	0.156	-103 -188	77.5	0.490
3	Solid sulphurous acid	0.325	-103 -188	75.2	0.228
3	Solid sulphurous acid	0.311	-103 -182.5	57.3	0.236

into liquid air, the range of temperature through which the body passes in one-third or one-fourth of a second is some 200°. Some of its heat will be lost to the vapour of the gas in the tube before it reaches the liquefied gas; and some at its various impacts on the walls of the glass-tubing, as it passes on to the calorimeter. The consequence of these losses will be to make the quantity of gas measured in the collecting receiver err by defect. Experiments were made with cooled substances to estimate the effect of a similar error in the opposite direction. It was found that 1 gm. of lead, ejected at the temperature of liquid air into the calorimeter filled with liquid air, absorbed enough heat on its passage to produce 1 c.c. of air in the gas receiver; roughly 1 gm. of lead falling through 200° into liquid air produced 100 c.c. of air in the receiver; hence, in this case, the error is within 1 per cent. A similar observation with diamond gave 1.8 c.c. in comparison with 150 c.c.—an error of about 1 per cent; and graphite gave some 4 c.c. in comparison with 300 c.c.—an error of about 1 per cent. Such errors may be neglected in these results.

The observations were reduced by comparison with lead. The method of comparison has obvious advantages. Each day when experiments were being made on any substance, a concomitant series was made on lead, so that unknown errors would affect the results equally, and thus produce volumes of gas in the receiver accurately proportional to the quantities of heat carried into the calorimeter. The choice of the particular metal in question was based on the following considerations:—The low specific heat of lead enabled small quantities of heat to be conveyed into the calorimeter, while the mass of metal was still considerable; the variations in the specific heat of lead with temperature are small, and are very nearly a linear function of the temperature; and, lastly, this metal is easily obtained very pure.

The values taken for the specific heat of lead were:—

	Specific heat.
Between -252.5° and -188° , or at -220.5°	$= 0.0280$
" -188.0° " -78° " -133.0°	$= 0.0290$
" -188.0° " $+18^{\circ}$ " -85.0°	$= 0.0295$

From calculations based on these values, an error of a degree in the first of these ranges would only affect the specific heat by 0.000006; a similar error in the second range would produce the same variation in the specific heat; and in the third range the variation would be 0.000004. Hence a variation of from 10° to 20° in any of these ranges would not affect the given values of the specific heat noticeably.

As a selection those given in Table II. may be taken as typical of the reduction of the diamond results.

The mean results of the experiments made with diamond, graphite, and ice are given in Table III. In the second column the number of experiments is given; the third column specifies the range of temperature through which the substance fell in giving up its heat at the lower temperature; the fourth column contains the mean specific heat of the substance calculated by comparison with that of lead, each separate experiment being compared with an immediately preceding or succeeding experiment with lead.

From the results given in Table III. are constructed the summary of specific heats stated in Table IV.

It appears from these values that between the ordinary temperature and the boiling-point of hydrogen the specific heat of the diamond has been reduced to $\frac{1}{3}$, whereas under similar conditions graphite has diminished to about $\frac{1}{6}$. Further it will be observed that at the lowest temperatures the specific heat of graphite is about three times that of the diamond. It is also worthy of being recorded that the values of the specific heats of diamond and graphite taken between the temperature of liquid air and boiling hydrogen are far smaller than that of any known solid substance, being even lower than that of any gas taken under constant volume.

Early determinations of the specific heat of carbon in any of its forms showed complete departure from the law

of Dulong and Petit. But all such experiments were in general made over a range of temperature from about the freezing-point of water to some 200° or 300° C. In April, 1872, Professor H. F. Weber read a paper on the specific heat of carbon before the Chemical Society of Berlin. I had made experiments on the same subject for the purposes of a paper read on April 1 of the same year before the Royal Society of Edinburgh, a continuation of which was read to the British Association in the following August. Both of these papers appeared in the *Philosophical Magazine* of 1872 (H. F. Weber, "The Specific Heat of Carbon," *Phil. Mag.*, 1872, Ser. 4, vol. xlv., p. 251; J. Dewar, "The Specific Heat of Carbon at High Temperatures," *Phil. Mag.*, vol. xlv., p. 461).

Professor Weber's observations extended from 0° to 200°, and led him to the conviction "that the specific heat of carbon in all its allotropic modifications varies to a considerable degree with the temperature." This he verified by finding that "the specific heat of the diamond is tripled when the temperature is raised from 0° to 200°." My own investigations at that time consisted of two groups, the first from 20° to the boiling-point of zinc, taken as 1040° C., and the second to the temperature of the oxy-hydrogen blowpipe, some 2000° C. I found that the mean value of the specific heat of gas-carbon in the first range was 0.32, and for the second range was 0.42, and I added "the true specific heat at 2000° must be at least 0.5; so that at this temperature carbon would agree with the law of Dulong and Petit." In 1875, Professor Weber published results (*Phil. Mag.*, 1875, Ser. 4, vol. xlix., p. 285), proceeding by a series of intermediate steps up to 1000°, and showing finally "that from the point (about 600°) at which the specific heat of carbon ceases to vary with increase of temperature, and becomes comparable with that of other elements, any real difference in the specific heats of the two modifications disappears, and carbon obeys the law of Dulong and Petit."

Professor Weber further showed that the specific heat of carbon, in both its forms, when plotted to temperature as abscissa, produced a curve with a point of inflection in it, like the Old English *f*. He found the point of inflection at about 60° C. for diamond and at about 0° C. for graphite (*Phil. Mag.*, vol. xlix., pp. 180, 279). The results given by Weber lead to Table V.

The close agreement between the result of the present investigation for diamond and Weber's result over the same range is noteworthy; the slight difference in the case of graphite may easily be accounted for by the difference in the graphites used. But in both cases the present results coincide with the trend of the curve as pointed out by Weber for low temperatures. The Weber formula for the diamond, namely,—

$$\text{Specific heat} = 0.0947 + 0.000994t - 0.00000036t^2.$$

if extrapolated would make the specific heat of diamond vanish about -92° C. Behn (*Ann. der Phys.*, 1900, Ser. 4, vol. i., p. 261) gives the specific heat of graphite between -78° and -186° as 0.075, which is much higher than the value given in Table IV.

Previous observations on the specific heat of ice are few, but the following have been noted:—

Regnault	-78° to 0°	0.4627
Person	-30° " 0°	0.505
Person	-21° " -1°	0.5017

These are in agreement with the first result for ice in Table IV.

The specific heat of ice between the temperatures of liquid air and liquid hydrogen has practically been reduced to about one-third the value between 0° and -78° , and has finally only about half the specific heat of steam at constant volume.

It was a matter of some interest to investigate the behaviour of various groups of substances, as regards their specific heats at low temperatures. In Table VI. the specific heats of two alloys are given, which were used in

the course of the present investigation; also those of the group of sulphur, selenium, and tellurium. Two alums, for which Kopp had made some observations, were included in the research, together with three other typical salts. Again, naphthaline and paraffin were a pair, whose specific heats were examined; also the chloride, bromide, and iodide of silver. The results for the solidified gases, carbonic acid, ammonia, sulphurous acid, were of obvious interest, and several observations on them are given. With regard to these bodies, it may be noted that the values found are not far removed from those of the specific heats at constant volume in the gaseous state, and I have no doubt that if the experiments had been extended to temperatures between that of liquid air and hydrogen these results would all have been below the gas constant. The other bodies examined all show diminution of specific heat at the lower temperatures, the most marked examples being the hydrocarbons, paraffin and naphthaline. An almost endless field of research in the determination of specific heats is now opened, in which the use of liquid air and hydrogen calorimeters are certain to become ordinary laboratory instruments.

(To be continued).

THE PRESSURE OF EXPLOSIONS. EXPERIMENTS ON SOLID AND GASEOUS EXPLOSIVES.*

By J. E. PETAVEL.

ALTHOUGH this subject has been dealt with by numerous investigators certain branches of it still remain practically untouched. With regard to the solid explosives used in ballistic work, the maximum pressure developed is usually well known, but the conditions which govern the combustion of the charge and the rate of cooling of the gaseous products require further investigation.

Explosive gaseous mixtures have only been studied at initial pressures but little above that of the atmosphere. Even in the case of coal-gas and air, which forms an exception to this rule, the work has not been extended to high pressures. The present research was undertaken with a view to filling in these gaps.

The first part of the paper describes the apparatus which was used for the investigation of both solid and gaseous explosives; the second part deals specially with the properties of cordite. The pressures are photographically recorded on a revolving cylinder by means of a specially constructed manometer. This manometer was designed with the object of securing the lowest possible time period.

The rise of pressure during the explosion of even the fastest cordite was, by means of this instrument, accurately inscribed without any oscillations being set up in the mechanism of the recorder. The pressures measured range from 100 to 1800 atmospheres (0.7 to 12 tons per square inch).

Many of the results obtained during the study of cordite are most easily expressed graphically, and a study of the curves given in the paper will be found preferable to the most careful abstract. In dealing with such a subject, general statements bereft of the necessary explanations and qualifications are apt to be somewhat misleading.

The present investigation confirms the view that the combustion of cordite proceeds according to parallel surfaces. The rate at which the flame travels towards the centre of each particle of explosive is proportional to the pressure under which combustion is taking place.

This velocity is measured, and it is shown how both the time required to reach the maximum pressure, and also the shape of the curve representing the rise of pressure, may be calculated from the data given.

The effect produced by decreasing the diameter of the explosive is discussed. Though the time required for complete combustion decreases with the diameter, the shape of the curve representing the rise of pressure remains practically unaltered, the scale of time alone being changed. Thus, even were the cordite in the finest state of division, though the combustion would be nearly instantaneous the effect produced would always be distinct from that of a detonation.

The maximum pressures obtained are compared with the measurements made by Noble, with which they are in close agreement. It is shown that the pressure developed by the explosion for various gravimetric densities may be deduced, with a fair degree of approximation, by formulæ derived from the kinetic theory of gases. The pressures calculated according to Van der Waals' law are compared with the experimental results.

The modifications introduced by the use of enclosures of different shapes are studied. When the surface of the enclosure is considerable as compared with its volume, the diameter of the cordite has a marked influence on the maximum pressure developed. For large diameters the pressure is considerably below the normal value.

With regard to the rate of cooling the results are compared with those obtained by the author in previous experiments on gases under high pressures (*Phil. Trans.*, A, 1901, vol. cxcvii., pp. 229 to 254). The investigation leads to the conclusion that the rate of cooling depends essentially on the thermal conductivity of the enclosure and not on that of the gas.

With the massive enclosures which are necessary for such experiments, it is found that the rate of cooling varies, not in proportion to the surface, but more nearly as the square of this value. Incidentally, attention is drawn to the very high temperatures which are reached by the inner surface of the steel walls. This throws some light on the important question of erosion.

When the explosion takes place in a long vessel, wave action is frequently set up. A non-uniform distribution of the explosive enhances this phenomenon. The velocity of the pressure-wave is measured and compared with the velocity of sound under similar conditions. Generally speaking, the work confirms the remarkable properties of cordite with regard to its high power and to the regularity of the effects produced.

The paper is accompanied by some 20 figures illustrating the results obtained, and is followed by tables giving the principal numerical values.

A QUICK METHOD FOR THE VALUATION OF FLUOR-SPAR.

By A. W. GREGORY.

THE method of determining the percentage of calcium fluoride present in fluor-spar by calculating from the increase in weight observed when a portion is treated with sulphuric acid and ignited, is unreliable when carbonates and silica are present.

The following modified procedure gives more reliable results, and incidentally the percentage of silica present may be quickly and accurately determined.

The sample is dried at 120° C.

1. Two grms. of the dried sample are then ignited at a red heat until the spar ceases to lose weight.

In most cases this loss in weight represents the CO₂ expelled, with sufficient accuracy for ordinary valuations.

Where great accuracy is required the CO₂ may be estimated by other methods.

2. A 2 gm. portion is treated with pure hydrofluoric acid in a tared platinum dish. After careful evaporation the spar is ignited and weighed. This operation is repeated until a constant weight is obtained.

* Abstract of a Paper communicated to the Royal Society.

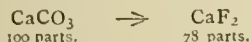
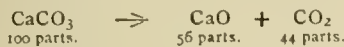
3. A similar weight of the spar is placed in a small platinum dish and tared.

Strong sulphuric acid is added cautiously, evaporated to dryness, and the residue ignited and weighed.

If the quantity of silica is considerable the residue must then be treated with hydrofluoric acid. Finally, however, the spar must be again treated with sulphuric acid and ignited.

The percentage of CO_2 may be calculated from operation No. 1.

In operation No. 2 the calcium carbonate will be converted into fluoride. If silica is entirely absent there will be a loss in weight exactly half of that obtained in operation No. 1; since—



whence the loss is equal to $100 - 78 = 22$ parts. The difference between the actual weight after the operation and the weight which may be deduced from operation No. 1 is equal to the amount of silica present. (When the silica is partly present as silicate this is not strictly true).

In the third operation there is an increase in weight due to the conversion of the calcium carbonate into calcium sulphate and of the fluoride into the same compound; there will also be a loss of any silica present.

The weight of silica obtained in operation No. 2 is added on to the final weighing in operation No. 3, and the increase in weight due to the formation of calcium sulphate from the carbonate subtracted. The remaining increase in weight is due to the conversion of the fluoride into sulphate, from which the percentage of calcium fluoride may be calculated.

THE AVAILABILITY OF MIXED FERTILISERS.

By W. F. SUTHERST, Ph.D., F.I.C.

ONE finds in agricultural practice that mixtures of manures are nearly always more beneficial than the use of, say, one—e.g., superphosphate—and one naturally concludes that it is in the ingredients of the mixed fertilisers that the soil is lacking, and consequently the crops are enabled to grow to greater advantage. According to Liebig's law of minimums, the plant grows in proportion to the ingredient present in the soil in the least quantity, so that phosphoric acid, nitrogen, potash, lime, &c., must be present in proportion found in the ashes of plants to enable the roots to take up their full capacity of inorganic matter.

From some experiments carried out by me, it seems that by mixing certain fertilisers together the availability increases in some cases and decreases in others. For instance, in nitrate of soda and bone flour together, the phosphoric acid in the bone flour is much more soluble in 1 per cent citric acid than when alone; this is also the case, to a less extent, when kainite, salt, &c., are mixed with it. When, however, bone-meal containing still a large quantity of organic matter is treated in the same way, less phosphoric acid is dissolved out than when alone. One might explain this by assuming that bone-meal, when in the soil, undergoes fermentation, by which the phosphoric acid is rendered more soluble, but when quantities of inorganic salts are present this fermentation is prevented.

The method for these experiments was as follows:—One grm. each of bone-meal and bone-flour were mixed with equal amounts of nitrate of soda, sulphate of ammonia, kainite, muriate of potash, &c., and, after moistening with water, allowed to stand about three weeks. At the end of that time the mass was treated with 1 per cent citric acid solution, and the amount of phosphoric acid extracted estimated by the molybdate method. The results obtained are given in the accompanying table.

Mixture.	Amount $\text{Ca}_3(\text{PO}_4)_2$ dissolved. Per cent.
Bone-meal + muriate of potash	26.54
" kainite	23.99
" salt	25.85
Bone-meal alone	29.06
Bone-flour + sulphate of ammonia	41.51
" muriate of potash	49.06
" kainite	47.97
" common salt	45.30
" nitrate of soda	67.70
" salt + nitrate of soda	44.77
Bone-flour alone	43.45

The Agricultural College, Tamworth.

NOTE ON TRIBO-LUMINESCENCE.

By C. S. STANFORD WEBSTER, F.I.C.

WHEN large crystals of artificially prepared salicylic acid are placed on flannel and crushed against a glass plate in the dark, on viewing it from the other side many brilliant flashes are seen to be emitted. With the natural acid only very few flashes make their appearance. The result is proportionately similar on shaking a little of the substances up violently in a bottle. Both artificial and natural salicylic acid respond to radium more than is usually the case with organic compounds possessing tribo-luminescence of the first order.

A convenient method of examining hard substances, both organic and inorganic, for tribo-luminescence, is to rub them on a sheet of ground-glass, viewing the effect from the smooth side; if the substance cannot be held with the fingers it is best placed on flannel for the purpose. The ground-glass may be advantageously fitted in a wooden frame with a handle, and held like a hand mirror; any of the powdered substance that adheres to the ground surface is easily removed with a wet cloth.

NOTE ON THE

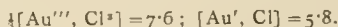
CAUSES WHY AN ELEMENT OFTEN PASSES FROM ONE GRADE OF COMBINATION TO ANOTHER WITHOUT GIVING RISE TO INTERMEDIATE COMPOUNDS.

By GEOFFREY MARTIN, B.Sc. (Lond.).

IN general, the intensity of the force with which atoms are attracted by an atom A when the latter is in different valency conditions, varies with the particular valency grade assumable by it. Sometimes the intensity of force exerted by A on each individual atom is greatest when A is in a high valency grade; sometimes it is greatest when in a low valency grade. Usually, however, the higher the valency grade which A finds itself in, the feebleer the force it exerts on other atoms. To give one example of this general fact, we will take the case of chromium.

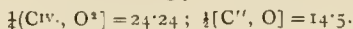
The chromium atom when in an octavalent state (Cr^{VIII}) exerts but a very feeble force on oxygen, CrO_4 evolving O at $20-25^\circ \text{C}$. In a hexavalent condition the force which the Cr atom exerts is considerably greater, CrO_3 evolving O at about 195°C . In a tetravalent condition the attraction which the Cr atoms exert is still greater, CrO_2 evolving O at 300° . Finally, in the trivalent condition the attractive force the Cr atoms exert on the O is enormous— Cr_2O_3 not parting with O even at the highest temperatures. The same phenomena is met with in the case of the majority of elements capable of existing in several valency grades of combination. Did the rule always hold true, it would be invariably easier to detach an atom from a

molecule containing many atoms attached to the central atom A than from one containing only a few atoms attached to A. But this is not always the case; for example, trivalent gold undoubtedly attracts chlorine with a greater force than monovalent gold. Thermal data shows this:—



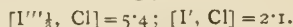
Also the chemical behaviour of AuCl_3 and AuCl leaves no doubt that AuCl_3 is the stabler of the two compounds— AuCl being the easier to decompose both by water and heat.

Similar cases are furnished by indium, In''' exerting a stronger force than In'' and In' , judged from the behaviour of the chlorides, InCl_3 , InCl_2 , InCl . C^{IV} attracts O and S more strongly than C^{II} :—



CS is decomposed into C and S at 200°C ; CS_2 is capable of standing a much higher temperature—showing that C^{IV} attracts S more strongly than C^{II} .

I''' attracts Cl more strongly than I' :—



The compounds of molybdenum, mercury, platinum, and ruthenium furnish further example.

This is the cause why high-grade compounds often decompose discontinuously into low grade compounds without giving rise to intermediate compounds. For example, MoO_3 when reduced by H passes directly into MoO_2 without giving rise to intermediate oxides, such as Mo_2O_5 or Mo_3O_8 . Rogers and Mitchell (*Journ. Am. Chem. Soc.*, 1900, xxii., 350—351) showed that Mo_3O_8 —an oxide intermediate between MoO_3 and MoO_2 —is more easily reduced in H than is MoO_3 or MoO_2 . This shows that Mo^{VI} and Mo^{V} attract O more strongly than Mo^{IV} ; so that any conditions which bring MoO_3 or MoO_2 to the point of decomposition would already have decomposed Mo_3O_8 . Similarly, MoO_2 when heated in H passes directly into Mo without producing any of the lower oxides, such as Mo_2O_3 , MoO , or Mo_2O . Mo^{IV} , in fact, in MoO_3 attracts the O more strongly than the Mo^{III} or Mo^{II} attracts it in Mo_2O_3 or MoO , and thus any influence which is capable of tearing away the O from Mo^{IV} in MoO_2 will still more easily remove it from Mo^{II} or $\text{Mo}_2^{\text{III}}\text{O}_3$ when O is not strongly attracted. For a similar reason $\text{Mo}^{\text{IV}}\text{S}_2$, when heated in a current of H, is reduced directly to the metal without forming a lower sulphide (Guichard, *Comptes Rendus*, 1899, cxxix., 1239—1242).

Again, I_2O_5 when heated decomposes at 300° directly into I and O without forming lower oxides. The reason, of course, is that the iodine atom when in the pentavalent state attracts the O atoms more strongly than when in a tetrad, triad, or monad state. So that when the temperature is high enough to detach the O from I^{V} in I_2O_5 , it will still more easily detach it from I^{III} in I_2O_3 , or I^{I} in I_2O . So that I_2O_5 passes directly into I and O without giving rise to I_2O_3 or I_2O . In fact, I_2O_5 decomposes at over 300°C , IO_2 at 170° , I_2O_3 at 125 — 130° (Watts' "Dict. of Chemistry," 1897, iii., 18); I_2O_5 is undecomposed by boiling water, whereas both IO_2 and I_2O_3 are decomposed. Similarly, CS_2 goes directly into C and S without giving CS.

The oxides of potassium, K_2O , KO , K_2O_3 , and KO_2 , and of chlorine, Cl_2O , Cl_2O_3 , ClO_2 , Cl_2O_7 , furnish similar phenomena.

As regards stability, the compounds of an element usually separate out into two groups—those of an odd grade of valency and those of an even. So that, in general, in the case of some elements (the so-called "artids"), the compounds of an odd type of combination are more stable than the compounds of an even type, whereas in the case of other elements (the so-called "perissads") the compounds of an even type are more stable than the compounds of an odd type.

Sometimes, indeed, so widely do these two classes of compounds differ for one and the same element, that while

representatives of the one class are known, representatives of the other are completely wanting. For example, no monovalent, trivalent, or pentavalent compounds of carbon are known, although divalent and tetravalent (CO , CS ; CO_2 , CS_2) are well known.

Again, the halogens produce monovalent (ClK), trivalent (I_2O_3), pentavalent (I_2O_5) and heptavalent compounds (Cl_2O_7)—all artid bodies—but the intermediate perissad compounds have not been obtained. Usually, however, representatives of both classes are known; indeed, in the case of Mo and W the perissad and artid compounds seem to be of nearly an equal degree of stability.

The whole phenomena arises out of the fact (due to an unknown cause) that the intensity of the force with which atoms are attracted by an atom A when in the grades of valence n , $n-2$, $n-4$, $n-6$, &c., are usually greater each to each, than the intensity of force with which it attracts atoms when in the intermediate grades of valence $n-1$, $n-3$, $n-5$, $n-7$, &c. So that the atom will pass directly from the grade of combination n to the grade $n-2$, $n-4$, &c., without producing the intermediate compounds of grade $n-1$, $n-3$, &c.

Of course all this holds only at normal temperatures; at high temperature the element may be most stable as perissad, although at ordinary temperatures it is most stable as artid; e.g., FeCl_3 and Fe_2O_3 are ordinary temperatures, are more stable than FeCl_2 and FeO ; but at a very high temperature FeCl_2 and FeO are more stable than FeCl_3 and Fe_2O_3 .

These examples I think throw light on the cause why an element does not give rise at a given temperature to compounds of every valency grade, but only to those of certain particular valency states.

I have long convinced myself by the study, extending over years, of the data relating to rare and imperfectly known compounds of elements, that every element is capable of giving rise to valency compounds of every grade between 1 and 8, but owing to the stronger attraction the elements, when in certain valency grades, exert on other atoms, most of these compounds at once spontaneously pass over into these stablest grades of union, and that the unstable grades of union are only revealable to us by accidental influences—such as the immersion of an element in a suitable medium, by altering the temperature and pressure under which we view the elements, &c.

By altering in a suitable manner the external conditions under which we view the element (such as the temperature, pressure, medium in which the element is immersed, and so on) we could probably cause an element to generate compounds of any valency grade.

Indeed, we may safely conclude that the unknown (because unstable) compounds which an element produces are enormously more numerous than the known (because stable). We are, in fact, only acquainted with a few compounds of an element whose stability under ordinary conditions of temperatures and pressure rises above a definite limit which enables them to exist unchanged for a time long enough for us to examine them chemically. The far greater multitude of unstable compounds remain completely unknown on account of the rapidity with which they go over into more stable forms of union. It is only the slow rate of change of the unstable into the more stable forms which enables such an enormous number of carbon compounds to exist simultaneously at ordinary temperatures in a state of very slow change. At a red or white heat the rate of change is so greatly increased that nearly the whole of organic chemistry is destroyed, and carbon then behaves like other elements in its capacity of giving only a few compounds of greater stability. If by any means, in the case of a given element, we could arrest or greatly diminish this rate of change of the unstable compounds into stable compounds, we would find the element produced compounds whose range and multitude rivalled those of the carbon compounds at ordinary temperatures. Perhaps low temperatures will give us this means.

This and other matters relating to affinity are discussed

in my work, "Researches on the Affinities of the Elements" (London, Macmillan and Co., 1905), to which for further information the reader is referred.

University of Kiel.

THE DEVELOPMENT OF SPECTRO-CHEMISTRY.*

By Professor JULIUS WILHELM BRÜHL, Ph.D., Sc.D.,
Hon. Mem. R.I., Professor in the University of Heidelberg.

(Concluded from p. 177)

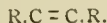
VI.

17. CARBON can thus act variously upon light according to the manner in which its atoms are combined. We can therefore transfer the refractive increment of the double bond to the atom itself.

In the diamond, and in all paraffinoid carbon compounds, the atomic refraction of carbon equals 5; it is therefore equal to 10 for two carbon atoms. The double bond increases the refraction by 2, so that for two carbon atoms with a double bond the refraction amounts to 12. The atomic refraction of one carbon atom with a double bond is therefore equal to 6, i.e., 20 per cent greater than that of the atom with the single bond:—

	Atomic refraction.
One carbon atom C (diamond and paraffins) . .	5
Two carbon atoms 2C (diamond and paraffins) . .	10
Double bond	2
Two carbon atoms with a double bond C=C . .	12
One carbon atom with a double bond C= . .	6

18. Carbon, being a quadrivalent element, can also appear with triple bonds:—



Experiment has shown that carbon with a triple bond also acquires a special atomic refraction.

Thus it becomes possible to establish the presence of this kind of bond in substances, and to distinguish it from the double and simple bonds—a further criterion of structure.

19. In consequence of these discoveries it became highly probable that all multivalent elements, such as carbon, possessed an atomic refraction varying with the kind of bond, while the univalent elements, such as hydrogen, display constant optic values, because atoms such as theirs can only be linked with a simple bond.

Later researches have confirmed this. The univalent halogens give, like hydrogen, constant atomic refractions, both in the elementary state and in their compounds. The multivalent elements, on the other hand, such as oxygen and nitrogen, display different optical values, according to the kind of bond.

In the course of such researches the behaviour of oxygen as a quadrivalent element, which had been previously conjectured, was established with certainty, and afterwards confirmed synthetically by Collie, Tickle, and others.

20. The theory which accounted for the optical abnormalities of certain classes of bodies, making them, in fact, abnormalities no longer, has proved extraordinarily fruitful. It formed the starting-point of all subsequent discoveries in the subject, and, indeed, we may describe the progress of this branch of science during the last twenty-five years as based essentially on this conception.

For not until we had fathomed the mystery of the benzene refractive increment 6, was it possible to know for certain that the variable valency of the multivalent elements is always of determining influence on the optical behaviour of bodies. Thus for the first time a spectrochemical method was called into being for the study of chemical structure,

and the foundations were laid of what we now call "Spectro-chemistry."

VII.

21. We must now return once more to the formula for refractivity. Newton's expression $\left(\frac{n^2-1}{d}\right)P$ had proved

not constant for the temperature in the case of fluid bodies, and was therefore replaced by Gladstone and Dale's more satisfactory ratio $\left(\frac{n-1}{d}\right)P$. For twenty years and more

this did admirable service. As, however, the number of observations kept on increasing, even this formula betrayed imperfections which finally led to its abandonment. It is impossible here to follow the argument in detail, and we must be content with the remark that comparisons of bodies in different states of aggregation failed to yield satisfactory constants. The values of $\left(\frac{n-1}{d}\right)P$ for a fluid or solid

substance always came out considerably greater than for the same substance in the state of gas or vapour.

22. Then by a happy chance two physicists, L. Lorenz, of Copenhagen, and H. A. Lorentz, of Leyden, came forward simultaneously in 1880 with a new expression for refraction. One of them started from the ordinary theory of light, the other from Maxwell's electromagnetic theory of light based on Faraday's views, and they both reached the same result, viz., that the true measure of refractivity is furnished by the expression—

$$\left(\frac{n^2-1}{n^2+2}\right)\frac{P}{d}.$$

Experimental tests showed that this theoretical expression was in fact, for all bodies, practically unaffected not only by temperature and pressure, but also by the state of aggregation.

Chemical tests confirmed the utility of the new optical standard, since the operation of all the laws before mentioned was observed to be even more exact when the new constant was applied.

23. Moreover, the expression for refraction proved valuable in another respect. It was found to be very suitable for measuring the dispersive power of bodies.

If n_v and n_r denote the refractive indices for the limits of the visible spectrum, i.e., for violet and for red light, the difference of the refractivities for these end-rays of the spectrum:—

$$\left(\frac{n_v^2-1}{n_v^2+2} - \frac{n_r^2-1}{n_r^2+2}\right)\frac{P}{d}$$

is the measure of the power of different bodies to disperse light—to broaden out the spectrum. This ratio proved to be constant as regards temperature, pressure, and state of aggregation.

Gladstone had already observed that dispersion, like refraction, was connected with the chemical nature of bodies. Quantitative relations were, however, only obtained when a constant for refractivity had been found. And then from the molecular dispersions of compounds the atomic dispersions of their elements were deduced.

We cannot enter here into the relations which were thus shown to exist between the chemical composition of substances and their power to disperse light. We need only remark that the case as a whole is analogous to that of refraction. Dispersion is, however, a still more sensitive and more constitutional property, and therefore in many cases it is specially adapted as an aid to research on chemical structure.

VIII.

24. It only remains to add a few remarks on the applications of spectro-chemistry in science and in practical life.

I have already shown the principles on which spectrochemical methods of examination in general can be applied to the solution of scientific problems, to the discovery of

* A Lecture delivered at the Royal Institution, May 26, 1905.

the chemical structure of single substances or whole classes of bodies.

Now there are a large number of substances, some of them artificially built up by synthesis out of their elements, some of them occurring in the vegetable and animal kingdoms, or even in inorganic nature, the structure of which is of remarkable delicacy and instability. Among them are, for instance, the so-called "tautomeric" compounds, hydrogen peroxide, and many other unstable compounds. Substances of this kind are of a very special interest, for in consequence of their tendency to change, they are the principal cause of metamorphoses, the unceasing circulation of matter, the eternal birth and decay that goes on in nature.

Research into the atomic structure of such bodies by purely chemical methods is often very difficult, and not seldom impossible, because, owing to their sensitive organisation, chemical interference leads either to changes in the grouping of the atoms, which cannot always be controlled, or even to total decomposition.

In such cases it is of course of the greatest value to be able to examine the constitution of the bodies without affecting them chemically; and spectrochemistry, as we have seen, gives us the means of doing so. By observing the behaviour of light on its passage through the various substances, we gain an insight into their structure without in any way disturbing it.

25. In the last ten years the spectro-chemistry of the nitrogen compounds has also made remarkable progress. Nitrogen is of the greatest importance as an essential constituent of the proteids, the alkaloids, and many other animal and vegetable products. But its high valency and the extraordinary variety of combinations into which it can enter with other elements, surround it with special complications. Regardless of these, however, the spectro-chemical examination of nitrogen compounds has already yielded useful results, especially in the study of the alkaloids. It is to be expected that this optical method will also be of use in the chemistry of the albuminoids, the study of which is now being prosecuted with so much vigour.

26. One class of substances of increasing importance both to science and to chemical industry is that constituted by the natural and artificial perfumes. An overwhelming majority of them consists of derivatives of the terpenes. We have already mentioned that Gladstone, in this subject also a pioneer, was the first to study the optical behaviour of the terpenes. Since then the explanation of the structure of these bodies and of a large number of rich natural perfumes derivable therefrom has been rendered easier by the use of spectro-chemical methods. Similar assistance has been rendered to the synthetic preparation of valuable scents, such as ionone, the artificial scent of violets. In every scientific laboratory and in every rationally conducted chemical factory where work is being done on perfumes, the spectrometer is now an indispensable testing instrument, and hence also an implement in industrial production.

IX.

27. When scientific research opens up new methods of observing nature, it is generally not long before a use is found for these methods in practical life. The need is soon felt of perfecting, and at the same time simplifying, the scientific apparatus. Efforts in this direction have not been wanting in the case of the spectrometer, and they have been crowned with the most brilliant success.

Professor Abbe, the distinguished physicist who died not long ago, and after him Dr. Pulfrich, constructed spectrometers on the principle of total reflection. These instruments are distinguished from those formerly in use by their extraordinary simplicity and convenience, and they allow also of much more rapid work.

Such instruments, known as total-reflectometers, have been made for the most exact scientific measurements, and also for medical and technical purposes. Special forms are in use for the examination of fats and oils, milk and

butter; to determine the amount of salt contained in salt solutions; the amount of alcohol and extractive matter in beer; for the examination of blood and albuminoids in pathological fluids, &c. Several of these ingeniously contrived instruments give not only the refractive index and the dispersion of a substance immediately, without any calculation, but also directly the percentage of dissolved matter, e.g., of alcohol and extractives in beer.

A number of such instruments from the celebrated factory of Carl Zeiss, of Jena, are here exhibited at my request.

I have now reached the end of my remarks. I have reviewed the development of spectro-chemical research since Newton's time, and we have seen that, although different nations have taken part in the work, a specially large share has fallen to British investigators. For this reason, as I said at the beginning of my discourse, it has been a special pleasure to me to be able to treat of such a subject before the Royal Institution.

There is a saying of Montesquieu's which I venture to hope has its application to this evening:—"Quand vous traitez un sujet, il n'est pas nécessaire de l'épuiser, il suffit de faire penser."

From Newton to our own day—a length of time which our planet takes to complete 250 revolutions round the sun—that is the period through which we have sped in sixty minutes. It will be readily understood that on such a rapid trip we have only been able to stop at one or two view-points, and have been obliged to content ourselves with a hasty survey. I thank you all for having ventured yourselves with me on such a hurried excursion, and I shall be happy if it has been conducted without mishap.

THE ESTIMATION OF SULPHITES BY IODINE.

By R. HARMAN ASHLEY.

VOLHARD'S method for the determination of sulphur dioxide and sulphites is accurate and reliable, but involves the inconvenience of making up every solution to be examined accurately to a standard volume of which portions are to be drawn from a burette and made to react with definite amounts of a standardised solution of iodine. The method consists in running the unknown sulphite or sulphurous acid solution into a known amount of a standardised solution of iodine, acidified with hydrochloric acid, to the disappearance of the iodine reaction with starch. This procedure rests upon the facts that the oxidation of sulphite is brought about in the acidified solution, and that, as Bunsen showed, no more than a small proportion of hydriodic acid should be present at the point at which the bodies are made to react. The reaction for the oxidation of sulphur dioxide proceeds normally in dilute solutions according to the equation $2\text{SO}_2 + 2\text{I}_2 + 4\text{H}_2\text{O} = 4\text{HI} + 2\text{H}_2\text{SO}_4$. In solutions too concentrated, however, the secondary reaction, $\text{SO}_2 + 4\text{HI} = 2\text{I}_2 + 2\text{H}_2\text{O} + \text{S}$, takes place, as Volhard has shown, and vitiates the indications (*Ann. Chem.*, cxxlii, 93).

To avoid the inconvenience of the Volhard method it has been proposed by Rupp to bring about the oxidation of sulphites by treatment with an excess of standardised iodine in a solution made alkaline by acid sodium carbonate, and then, after fifteen minutes, to titrate the excess of iodine by sodium thiosulphate (*Ber.*, xxxv., 3694). This procedure, however, is, as has been shown by Ruff and Jaroch (*Ber.*, xxxviii., 409) and by the present writer (*Am. Journ. Sci.*, xiv., 237), faulty in principle and practice, and gives correct results only by a chance balancing of opposing errors. Theoretically it might be possible to overcome the difficulties by treating with acid the alkaline mixture of iodine and sulphite and acid sodium carbonate before attempting to titrate by sodium thiosulphate the excess of iodine.

In the experiments recorded in the table the following

procedure was followed:—The sulphite was treated with 1 grm. of acid sodium carbonate and an excess of standardised iodine solution. The solution was then acidulated with a safe amount of hydrochloric acid, it having been found by experiment that the presence of 10 c.c. of 1:4 hydrochloric acid in 125 c.c. of water was without effect upon the determination of iodine by sodium thiosulphate. The excess of iodine after acidification was titrated by standardised sodium thiosulphate. It will be noticed that, in the experiments recorded under A of the table, the excess of iodine used was small, and in these experiments large negative errors are obtained; while in the experiments recorded under B, in which a large excess of iodine was employed, the results are better. They are best when at least twice as much iodine is added as is theoretically required to oxidise the sulphur dioxide. The length of time during which the iodine may act does not affect the results to any very marked degree.

Iodine value of SO ₂ taken.	Iodine taken.	Iodine value of Na ₂ S ₂ O ₃ used.	Error in terms of—		Excess of HCl (1:4).	Vol. at titration.
Grm.	Grm.	Grm.	Iodine.	SO ₂ .	C.c.	C.c.
A.						
0.2197	0.3143	0.0978	-0.0032	-0.0008	7.5	125
0.2197	0.3143	0.0965	-0.0019	-0.0005	7.5	125
0.2197	0.3143	0.0970	-0.0024	-0.0006	7.5	125
0.1535	0.1913	0.0464	-0.0086	-0.0022	7.5	125
0.1535	0.1913	0.0467	-0.0089	-0.0022	7.5	125
0.1535	0.1913	0.0472	-0.0094	-0.0024	7.5	125
0.1535	0.1913	0.0465	-0.0087	-0.0022	7.5	125
0.2366	0.3194	0.0903	-0.0075	-0.0019	7.5	125
0.2906	0.3825	0.1132	-0.0213	-0.0054	7.5	125
0.3825	0.4463	0.0750	-0.0112	-0.0028	7.5	125

B.						
0.1143	0.3143	0.1990	+0.0010	+0.0003	5.0	125
0.1143	0.3143	0.1982	+0.0018	+0.0004	5.0	125
0.1143	0.3143	0.1992	+0.0008	+0.0002	5.0	125
0.1143	0.3143	0.1986	+0.0014	+0.0003	5.0	125
0.1482	0.3187	0.1708	+0.0003	+0.0001	7.5	125
0.1576	0.3187	0.1586	+0.0025	+0.0006	7.5	125
0.1576	0.3187	0.1643	+0.0032	+0.0008	7.5	125
0.1576	0.3187	0.1598	+0.0013	+0.0003	7.5	125
0.1576	0.3187	0.1606	+0.0005	+0.0001	7.5	125
0.1576	0.3187	0.1602	+0.0009	+0.0002	7.5	125
0.1576	0.3187	0.1622	+0.0011	+0.0003	7.5	125
0.1560	0.3195	0.1660	-0.0025	-0.0006	7.5	125
0.1992	0.4460	0.2482	+0.0014	+0.0003	7.5	125
0.1913	0.3825	0.1919	+0.0009	+0.0002	7.5	125
0.2056	0.3771	0.1701	+0.0014	+0.0003	7.5	125
0.2056	0.3771	0.1697	+0.0018	+0.0004	7.5	125
0.2056	0.3771	0.1707	+0.0008	+0.0002	7.5	125
0.2056	0.3771	0.1709	+0.0006	+0.0002	7.5	125
0.2131	0.4470	0.2412	+0.0073	+0.0018	7.5	125
0.2354	0.3825	0.1490	-0.0019	-0.0005	7.5	125
0.2597	0.4463	0.1869	-0.0003	-0.0001	7.5	125
0.2638	0.4463	0.1847	-0.0022	-0.0005	7.5	125
0.2908	0.6375	0.3505	-0.0038	-0.0009	7.5	125
0.3187	0.4463	0.1326	+0.0050	+0.0012	7.5	125
0.3395	0.6275	0.2842	+0.0038	+0.0009	7.5	125
0.3395	0.6275	0.2852	+0.0028	+0.0007	7.5	125
0.3395	0.6275	0.2844	+0.0036	+0.0009	7.5	125
0.3395	0.6275	0.2855	+0.0025	+0.0006	7.5	125

sufficiently large excess; nor does the theory of the catalytic action of iodine explain the fact that when a greater mass of iodine is used, under conditions otherwise similar, we get a larger oxidation of sulphur dioxide.

The most obvious explanation is that, at a low concentration of iodine, an intermediate oxidation product may be formed, and that the formation of this product may be prevented by sufficient concentration of the iodine. It is not unreasonable to suppose that the formation of a small amount of dithionate instead of sulphate is the occasion of the deficient expenditure of iodine noted when the concentration of this element is low, and that the dithionate is not formed appreciably when the iodine concentration is high. The dithionate once formed is but slowly attacked by iodine, and that is apparently the reason why long standing of the mixtures containing a small proportion of iodine does not result in complete oxidation of the sulphite to sulphate. From these considerations, it will be seen that the secondary error of Rupp's process may very probably be due to the formation of some dithionate from the sulphite where the concentration of the iodine is low.

The practical estimation of sulphurous acid or a soluble sulphite may, then, be accomplished with a reasonable degree of accuracy by adding to the solution of the substance, not exceeding 100 c.c. in volume and containing a grm. of acid sodium carbonate, at least twice as much iodine as is theoretically necessary to effect oxidation, acidifying cautiously with hydrochloric acid, and determining with standard sodium thiosulphate the excess of iodine remaining in the acidified solution.

The author takes this occasion to thank Prof. F. A. Gooch for much kind assistance.—*American Journal of Science*, vol. xx., p. 13.

NOTICES OF BOOKS

Chemistry for Engineers and Manufacturers. By BERTRAM BLOUNT, F.I.C., and A. G. BLOXAM, F.I.C. Vol. II. London: Charles Griffin and Company, Ltd. 1905.

The second volume of this work deals with the chemistry of manufacturing processes, and gives a good review of the general principles underlying the most important chemical industries. The book has been carefully revised for the second edition, and a large amount of new and valuable matter has been added, but otherwise its general scope and scheme have been retained. It will be found a useful and practical book of reference, especially for chemical engineers.

Second Year Chemistry. By EDWARD HART, Ph.D. Easton, Pa.: The Chemical Publishing Co. 1905.

The order in which the subjects are treated in this book is a serious defect, and one which will undoubtedly restrict its use in this country. Thus, after introductory chapters on molecules and atoms and the properties of gases, gas analysis is taken up, and then dissociation in solutions and electrolysis are discussed. Chapters then follow on the chemical balance, and very brief courses of volumetric and gravimetric analysis are introduced. Schemes for the detection and separation of the non-metals and metals are then given, a return being finally made to quantitative work in a few technical analyses. Although most teachers will agree with the author in recognising the importance of giving the beginner some practice in quantitative work before he proceeds to qualitative analysis, the method he has adopted to attain this object does not seem likely to lead to success. The early performance of simple quantitative estimations undoubtedly impresses upon the student the necessity for care in working, and has an important influence upon his later work in analysis, but it would not appear advisable to begin with gas analysis, which is better postponed until considerable dexterity in quantitative work has been acquired. As for the text, the directions for the

Ruff and Jaroch (*loc. cit.*) take the ground that, in the favourable results occasionally obtained by Rupp's process, an error due to the over-oxidation of the tetrathionate normally formed in the action of sodium thiosulphate upon the residual iodine is apparently balanced by some oxidation of sulphur dioxide by dissolved air, the iodine in solution acting catalytically as well as directly. The theory, however, is quite at variance with the evidence supplied in the table; for, if it were true, under no conditions could iodine in the presence of air act as a correct measure of sulphur dioxide, as it apparently does when used in a

experiments are clearly expressed and the methods appear to be well chosen. The chapter on chemical arithmetic gives very briefly the essentials of the subject, and a collection of examples for working is added, while general questions are interspersed throughout the text.

Kristallinische Flüssigkeiten und Flüssige Kristalle. ("Crystalline Liquids and Liquid Crystals"). By Dr. RUDOLF SCHENCK. Leipzig: Wilhelm Engelmann. 1905.

In Lehmann's work on liquid crystals the investigation of doubly refracting liquids under the microscope is discussed at great length, but the physico-chemical aspects of the investigations are only briefly alluded to; this book, on the other hand, describes the author's quantitative measurements of anisotropic liquids, and may thus be regarded as a supplement to Lehmann's larger work. The author gives an account of the preparation and properties of his material, and the investigation of the properties of the melting- and clearing-points, and has also collected a large number of measurements relating to viscosity, molecular surface energy, specific heat, and dielectric constants; from these measurements important conclusions can be drawn regarding the nature of crystalline liquids. For the sake of completeness, and to give the reader some insight into the optical behaviour and structure of anisotropic liquids, a short account of Lehmann's work is also included.

Thermodynamik Technischer Gasreaktionen. ("The Thermodynamics of Technical Gas Reactions"). By Dr. F. HABER. München and Berlin: R. Oldenbourg. 1905.

This book is written from a somewhat novel point of view; it does not aim at providing a complete treatise of thermodynamics, but at expounding the subject from a technical point of view, constant reference being made to technical examples. While a knowledge of chemistry and technology is presupposed, the amount of mathematics introduced into the text is reduced to the lowest limit possible. The work is in the form of seven lectures, in which the theory of thermodynamics, based upon the method developed by Helmholtz, is considered in detail; starting from elementary notions concerning the latent heat of chemical transformations, the reader passes by easy stages to the more difficult conception of the meaning of entropy, and thereafter to the practical application of the relations deduced from theoretical considerations. One lecture is devoted to a description of methods of determining the specific heats of gases and of the experiments performed by many investigators in this field, while the last lecture deals with relations which are of importance in determining gas equilibria, especially at high temperatures. The addition of a good index would be a great boon to those who use the book.

CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 11, September 11, 1905.

This number contains no chemical matter.

No. 12, September 18.

The Isolation of Terbium.—G. Urbain.—Inserted in full.

No. 13, September 25.

This number contains no chemical matter.

Berichte der Deutschen Chemischen Gesellschaft.

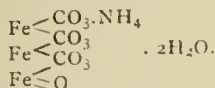
Vol. xxxviii., No. 12, 1905.

Sulphammonium and its Relations to Nitrogen Sulphide.—Otto Ruff and Emil Geisel.—When sulphur is dissolved in liquid ammonia a blue liquid containing sulphammonium is formed. Moissan has shown that this liquid is not a simple solution of sulphur, but that a chemical compound is formed, to which he ascribed the formula $(\text{NH}_3)_2\text{S}(\text{NH}_3)_2$ or $(\text{NH}_3)_2\text{S}(\text{NH}_3)$. The authors have found that a reversible reaction occurs, as represented by the equation $10\text{S} + 4\text{NH}_3 \rightleftharpoons 6\text{SH}_2 + \text{N}_4\text{S}_4$. The sulphuretted hydrogen formed may be precipitated with silver iodide, and from the residue nitrogen sulphide may be obtained, and thus a new synthesis of the latter is afforded. If a solution of nitrogen sulphide in liquid ammonia is treated with sulphuretted hydrogen the reverse reaction occurs. It is noticeable that in this case, although the solution contains dissolved sulphur, it is not blue but yellowish red. This is due to the presence of excess of ammonium sulphide, which decolourises the solution, dissolving the sulphur to polysulphides. The purplish blue colour of the solution of sulphammonium is probably due to a colloidal solution of elementary sulphur in ammonia and to the products forming during the reaction between sulphur and ammonia. The dichroism of sulphammonium is also possibly an argument in favour of the colloidal nature of the dissolved sulphur, although this same property has also been observed in the case of a number of other solutions which are probably not colloidal.

Organo-metallic Compounds.—Iwan Shukoff.—Diethyl thallium chloride, $\text{Ti}(\text{C}_2\text{H}_5)_2\text{Cl}$, is a strong electrolyte, which, however, in a high state of dilution may be hydrolysed to an appreciable extent. When a solution of $\text{Ti}(\text{C}_2\text{H}_5)_2\text{Cl}$ is electrolysed between two platinum electrodes, at the cathode metallic thallium is separated in crystals, and a gas is given off. It was therefore concluded that thallium ions are present as well as organo-metallic cations, and are formed from them by dissociation. From potential measurements it was found that the concentration of the thallium ions would work out to $10^{-2.07}$ for 0.0161-n TiCl , and to $10^{-2.78}$ for 0.0161-n $\text{Ti}(\text{C}_2\text{H}_5)_2\text{Cl}$, if Nernst's formula for the system $\text{Ti-meth.}-\text{Ti-salt}$ solution is assumed to hold good, which, however, is not certain. Thus from the potential measurements the only conclusion that can be drawn is that the monovalent thallium alkyl cation acts like a complex ion, which separates off Ti-ions to about 1/300 of its concentration. As regards the gaseous product of dissociation, it was found that it burns with a luminous flame, and consists of a mixture, in which about 15 per cent of unsaturated hydrocarbons may be detected by absorption with bromine water.

New Class of Iron Compounds.—Otto Hauser.—Some iron salts (both ferrous and ferric) are fairly easily soluble in excess of ammonium carbonate solution. From ferrous salts under suitable conditions an iron ammonium carbonate of the formula $\text{Fe}_{27}(\text{NH}_4)_3(\text{CO}_3)_3\text{Fe}_{11}\text{O}_2\text{H}_2\text{O}$ can be obtained, and this represents a new type of iron compounds. When excess of ammonium carbonate is added to a solution of a ferric salt, a red precipitate is first formed, and dissolves to a blood-red liquid, in which the iron may be precipitated by $-\text{SH}'$, by calcium chloride, and by boiling with alkalis, but not by a specific ferric ion reagent, such as potassium ferrocyanide. Ammonium carbonate dissolves Prussian-blue, giving a violet-red solution. The iron in such solutions is present as a complex ion. On evaporation, even slowly in the cold, the ferri-ammonium carbonate solution deposits ferric hydroxide, but in closed vessels it will remain unaltered for weeks. The precipitate formed in solutions of ferrous salts by means of ammonium carbonate is more difficultly soluble in excess of the reagent, the solutions being nearly or quite colourless when freshly prepared. They absorb oxygen from the air, and then deposit nearly all their iron in the form of a difficultly soluble greenish white precipitate. This precipitate appears under the microscope to consist of small

double refracting prisms, often forming star-shaped masses. These crystals rapidly darken in air; in dilute acids they dissolve, giving off carbon dioxide, and forming yellowish green solutions. Alkalis separate from them a black strongly magnetic ferroso-ferric oxide, ammonia being given off. Thus the salt is a basic ferri-ferro-ammonium carbonate of formula $\text{Fe}^{2+}(\text{NH}_4)(\text{CO}_3)_3\text{Fe}^{3+}\cdot 0.2\text{H}_2\text{O}$. The constitutional formula appears to be—



It is noteworthy that all the ammonia determinations gave too low a value for ammonia; this is probably due to incipient dissociation. Slow oxidation of the salt gives an olive-green powder in which the proportion $\text{Fe}^{2+} : \text{Fe}^{3+}$ is 1 : 1, but the author has not yet determined whether this is a single salt.

Phosphorus Pentasulphide.—Alfred Stock and Kurt Thiel.—If white phosphorus, sulphur, and a little iodine are dissolved in carbon disulphide, the solution filtered and heated for twelve hours to 120° – 130° in a steel tube, crystals of phosphorus pentasulphide are obtained, which may be purified from traces of sulphur, iodine, and iron by Hofmann and Stock's method (*Berichte*, 1903, xxxvi., 314). Stock and v. Schonthan noticed that the greater part of the pentasulphide thus prepared melts at 255° , while the melting-point of ordinary phosphorus pentasulphide is 275° – 276° . Hence they concluded that a second modification of P_2S_5 exists, probably of lower molecular weight than the ordinary variety. The authors have now confirmed this assumption, and find that of the two modifications the new variety is more soluble in carbon disulphide than the ordinary modification. They have investigated the molecular weight of the ordinary sulphide, by determining the raising of the boiling-point in carbon disulphide solution, and have found that the formula in boiling CS_2 is P_4S_{10} . Similar experiments with the new variety show that it contains a substance which has a smaller molecular weight than P_4S_{10} , but on the basis of the molecular weight determinations, and also from the fact that the new variety does not possess a sharp melting-point, it seems probable that it is not a single substance, but that it cannot be further decomposed by fractional crystallisation from carbon disulphide. The following table compares the two modifications:—

	Ordinary pentasulphide.	New variety.
Preparation.	Repeated crystallisation of the raw sulphide from hot CS_2 .	Rapid condensation of vapours of ordinary sulphide, washing with CS_2 , and crystallising the solution.
Appearance	Light yellow crystals, fairly stable in air.	White crystals, giving off H_2S in the air.
Solubility in boiling CS_2	1 : 195.	1 : 30.
Density	2.03.	2.08.
M. p.	275° – 275° .	Greater part melts at 255° ; entirely fused at 275° .
Mol. wt. in boiling CS_2	444, i.e., P_4S_{10} .	Abt. 360, i.e., between P_2S_5 and P_4S_{10} .

MEETINGS FOR THE WEEK.

WEDNESDAY, 25th.—Society of Dyers and Colourists, 8. "The Dyeing of Wool Mats," by J. W. Lamb.

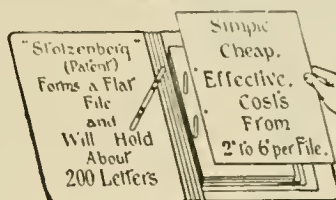
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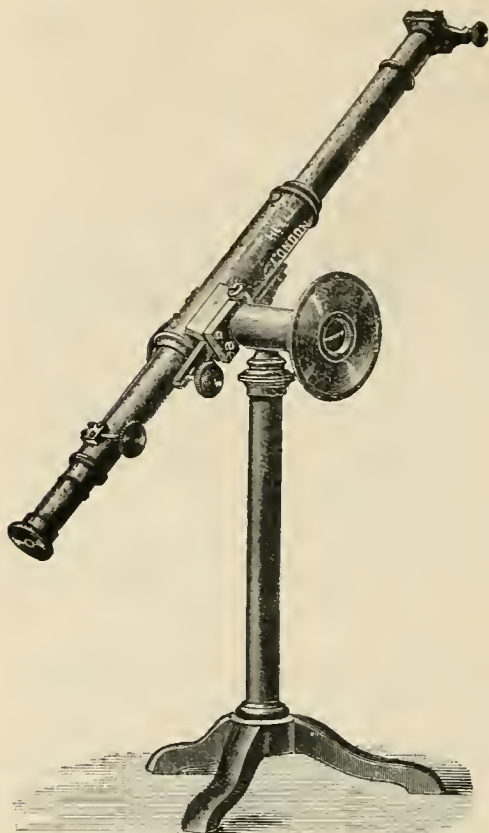
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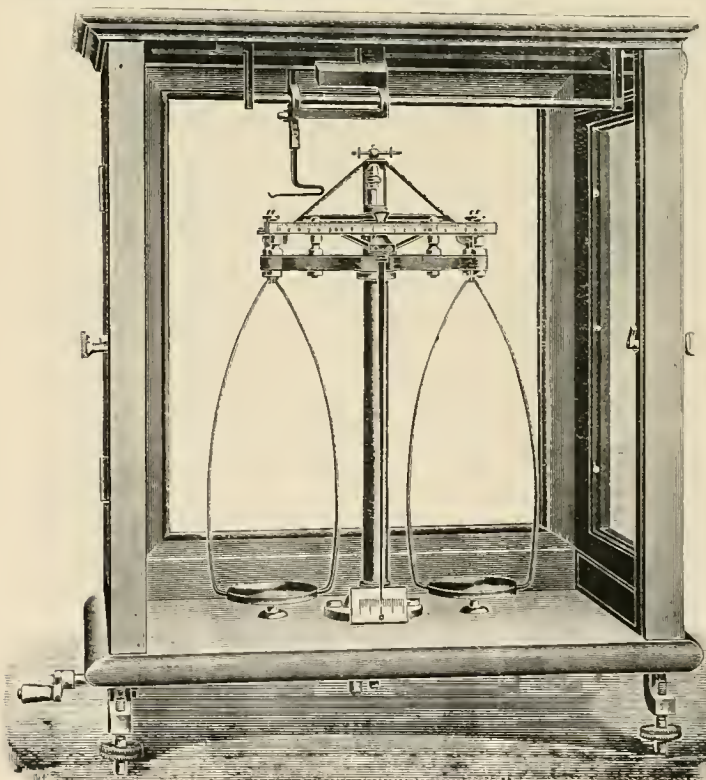
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STUDIES WITH THE LIQUID HYDROGEN AND AIR CALORIMETERS.*

By Sir JAMES DEWAR, M.A., LL.D., Sc.D., F.R.S., Professor of Chemistry at the Royal Institution, and Jacksonian Professor, University of Cambridge.

(Concluded from p. 184.)

11. Latent Heats.

IN the course of my experiments on the specific heat of diamond, graphite, and ice by means of the liquid hydrogen and air calorimeters, the frequent determination of the quantities of gas evaporated by lead in the same circumstances as the diamond, graphite, or ice under investigation afforded means for the direct measurement of the latent heats of hydrogen, nitrogen, oxygen, and air at their respective boiling-points. The same data for lead† were adopted as were used on the former occasion. The volumes of gas evaporated had, however, to be reduced to 0° C. and 760 m.m. of pressure. If C be the number of cubic centimetres of gas evolved per grm. of lead, measured at 0° C. and 760 m.m., while the lead cools from t'' to t' ,

m the number of grms. mass of gas per c.c. under standard conditions, and s' the mean specific heat of lead between t'' and t' , then L, the latent heat of the gas, is given by—

$$L = \frac{t' - t''}{m C} s'.$$

Table VII. contains a summary of the results obtained.

The details of three sets of observations show how closely the results are in accord. (See Table VIII.).

The latent heat of hydrogen, determined from these nineteen observations—some through the short fall of temperature from liquid air, some through the much larger fall from ordinary temperatures—may be taken as very closely 123 grm.-calories. Considering the great mobility of liquid hydrogen, and its small density, it might be imagined that some spray would get carried up by the hollow enclosing gas bubbles. If this took place in the experiments, then the latent heat would be too small. In like manner any solid air carried down from the neck of the calorimeter would have an effect of the same kind. If, however, the transit of the lead into the liquid hydrogen was impeded by a solid air constriction in the neck, or above, then the latent heat would be increased.

In my Bakerian Lecture, the latent heat of hydrogen was taken to be about 200 units, from which I made the following deduction (*Proc. Roy. Soc.*, June, 1901, lxviii., p. 361):—"The order of the specific heat of liquid hydrogen has been determined by observing the percentage of liquid that has to be quickly evaporated under exhaustion in order to reduce the temperature to the melting-point of hydrogen, the vacuum vessel in which the experiment is made being immersed in liquid air. It was found that in the case of hydrogen the amount that had to be evaporated was 15 per cent. This value, along with the latent heat of evaporation, gives an average specific heat of the liquid between freezing- and boiling-point of about 6." The

TABLE VII.

Substance.	No. of expts.	Fall of temperature.	Latent heat.	Mean.
Oxygen	6	17° to -182.5°	51.72	51.15
	3	16.4 -182.5	51.08	
	5	-78 -182.5	50.65	
Nitrogen	3	18.4 -195.5	50.4	50.4
	4	17 -195.5	48.1	
	4	-78 -195.5	52.7	
Hydrogen	5	17 -252.5	122.9	123.1
	4	17 -252.5	123.6	
	4	-188 -252.5	124.3	
	6	-188 -252.5	121.5	

TABLE VIII.

Weight of lead.	Volume of gas.	Gas per grm. of lead.	Mean.	Reduced to 0° C. and 760 m.m.	Latent heat.
Grm.	C.c.	C.c.			
Oxygen.—From -78° to -182.5°; Barometer, 760.9 m.m.; Temperature, 16.4°.					
1.529	67	43.83	44.30	41.84	$LO = \frac{104.5^{\circ} \times 0.0290}{0.00143 \times 41.84} = 50.65$
1.503	67	44.58			
1.545	68	44.01			
1.431	64	44.73			
1.567	69.5	44.35			
Nitrogen.—From 18.4° to -195.5°; Barometer, 760 m.m.; Temperature, 18.4°.					
0.471	50	106.2	106.3	99.59	$LN = \frac{213.9^{\circ} \times 0.0295}{0.001257 \times 99.59} = 50.41$
0.641	68	106.1			
0.657	70	106.5			
Hydrogen.—From 16.4° to -252.5°; Barometer, 753 m.m.; Temperature, 16.4°.					
0.160	117	731.2	760.5	710.8	$LH = \frac{268.9^{\circ} \times 0.0291 \times 1000}{0.0896 \times 710.8} = 122.92$
0.147	116	789.0			
0.122	94	770.5			
0.147	112	761.9			
0.104	78	750.0			

* A Paper read before the Royal Society, June 8, 1905.

† Behn (*Ann. d. Physik.*, 1900, [4], i., p. 261) gives specific heat of lead as 0.0300 from 18° to -79°, and 0.0291 from -79° to -186°, whence we get 0.0295 from 18° to -186°. From 100 to 18° he gives the value 0.0310, but adds that this is the "mean of known results." Later Schmitz (*Proc. Roy. Soc.*, 1903, lxxii., p. 192) gives the specific heat of lead as 0.0293 at -85°, and 0.0305 at +60°.

result of the present investigation enables me to correct this statement, the specific heat of the liquid between the boiling- and the freezing-point being 3.4 instead of 6. It appears, therefore, that hydrogen, instead of following the law of Dulong and Petit, has an atomic heat of only half the required amount. In my paper on "The Physical Constants of Hydrogenium" (*Trans. Roy. Soc. Edin.*, 1873), it was shown that the specific heat of hydrogen absorbed in palladium was at least 3.5. It seems therefore that hydrogen in the gaseous, the occluded, and the liquid condition has substantially the same specific heat.

In the Bakerian Lecture (*loc. cit.*), I noted for comparison with the specific heat of liquid hydrogen that when liquid nitrogen was similarly treated, "the resulting specific heat of the liquid came out 0.43, or about 6 per atom." Alt, in a recent direct determination of this quantity, gives the value 0.430 (*Ann. d. Physik.*, April, 1904, [4], xiii., p. 1027). This corroboration of the old determination of the specific heat of liquid nitrogen by the evaporation method, adds confirmation to the value now found for the similar constant for hydrogen.

Further corroboration of this value of the latent heat of hydrogen is afforded by Clapeyron's equation,—

$$\text{Latent heat} = (v - u) t \frac{dp}{dt};$$

where v and u are the specific volumes of the gas and the liquid at temperature (absolute) t and pressure p . With this equation we must combine either a Rankine or a Willard Gibbs relation between vapour pressure and temperature. From some early observations with the helium thermometer on the vapour pressure of hydrogen below its boiling-point, I found the Rankine equation—

$$\log p = 5.5038 - \frac{53.13}{t}.$$

Hence, noting that the density of liquid hydrogen at the boiling-point is 0.07, and the specific volume of the gas at the same temperature is 818.7 c.c., Clapeyron's equation gives 120.3 as the latent heat of liquid hydrogen.

A corresponding mean Rankine formula, based on Travers' smoothed results (*Phil. Trans.*, 1902, A, cc., p. 169), gave the latent heat as 119. On the other hand, two Willard Gibbs' equations, calculated from actual observations as evenly distributed as possible, gave the results 123.4 and 117.5, or a mean of 120.5. Thus, while theoretical results seem somewhat lower than those of observation, both point to a value of the latent heat of hydrogen about 121 or 122 grm.-calories.

In the case of nitrogen the observations seem equally good, and we get its latent heat about 50.4 grm.-calories. Determinations of this quantity by former observers are in very fair accord with this value. A careful investigation by Fischer and Alt gave 48.9 (*Ann. d. Physik.*, 1902, [4], ix., p. 1180), and more recently Alt (*Ibid.*, 1904, [4], xiii., p. 1024) gives 48.7 at 718 m.m. pressure (-196.2°) and 52.07 at 96 m.m. pressure (-210.05°). Again, Shearer found in two series of experiments the slightly higher value 49.8, a result (he says) which "agrees very well with that computed from the vapour tension which gives 49.25" (*Phys. Rev.*, 1903, xvii., pp. 124, 471).

From observations of my own on the vapour density of nitrogen between the boiling- and melting-points, I deduced a Rankine formula,—

$$\log p = 6.6462 - \frac{292}{t},$$

which leads to 48.03 for the latent heat of the liquid. In similar circumstances from Fischer and Alt's results, I find the value to be 49.65, while a Willard Gibbs formula from the same observations gives 51.4. The ratio of the liquid to the gaseous volume at the boiling-point being only 1/177, the correction on this account may be neglected in using Clapeyron's equation.

The value of the latent heat of oxygen is found to be 51.15 grm.-calories, the result of fourteen observations, with a possible divergence of half a calorie each way.

Among the most recent determinations of the latent heat of oxygen, Shearer gives the results of two series of observations as 60.9 and 61.0, and adds 60.8 as the result of "thermodynamic computation" (*Phys. Rev.*, 1903, xvii., pp. 124, 469—475). Estreicher, by an electric method, finds this quantity to be 58 calories per grm. (*Acad. Sci. Crac.*, 1904, *Bull.* 3, pp. 183—186; *Science Abstracts*, "Physics," June, 1904, No. 1441). These results are so high compared with other determinations that they must be received with some caution. A direct and careful series of observations by Alt (*Ann. d. Physik.*, 1904, [4], xiii., p. 1020), also by an electric method, gives 52.07 as the latent heat of oxygen at -182.8° (pressure 725 m.m.), rising to 58.85 at -201.3° (pressure 68 m.m.).

Olzowski, Estreicher, and Travers have made observations on the vapour density of oxygen which enable us to calculate its latent heat. Three Willard Gibbs' equations were calculated from Olzowski's observations between the critical-point and the boiling-point, from which a mean value of 51.4 was found (*Comptes Rendus*, 1885, vol. c., p. 351; *Nature*, 1895, vol. li., p. 355; *Phil. Mag.*, 1895, vol. xl., p. 210). A careful examination and selection from Estreicher's three sets of observations between the boiling- and the melting-point led to a Willard Gibbs' equation from which the latent heat was found to be 52.53 (*Phil. Mag.*, 1895, vol. xl., pp. 458, 459). From Travers' smoothed results a series of six Rankine formulae was calculated between 90.7° and 79.17° (absolute), from which the mean value of the latent heat was found to be 53.78 (*Phil. Trans.*, 1902, A, vol. cc., p. 152). The ratio of the liquid to the gaseous volume of oxygen at its boiling-point being only 1/255, its effect in the Clapeyron equation may be neglected.

As between oxygen and nitrogen it would appear that the former has the greater latent heat, a result to be expected if we rely on the constancy of Trouton's constant, namely, that the molecular latent heat is proportional to the absolute temperature of the boiling-point. We may determine the ratio of these two latent heats independently of the value of the specific heat of lead, by selecting observations over approximately the same range of temperature, for we have noted how slight is the variation of the specific heat of lead per degree of temperature. On examining the details of the possible sets of observations that may be compared, I select the set for nitrogen in which a mean of 106.3 c.c. of gas per grm. were given off. This, reduced to 0° and 760 m.m., became 99.59 c.c., over a range of temperature from 18.4° to -195.5° . Two sets of oxygen observations seem equally good, namely, the first two. In the former of these the mean volume of gas given off per grm., reduced to 0° and 760 m.m., was 79.38 c.c., over a range of temperature from 17° to -182.5° ; and in the latter 80.34 c.c. were given off in the same standard circumstances over a range from 16.4° to -182.5° .

Combining these last two with their relative weights of 6 and 3, we get, putting s' for the specific heat of lead, and w for the weight of 1 c.c. of hydrogen,—

$$LO = \frac{198.9^\circ + 2 \times 199.5^\circ}{(80.34 + 2 \times 79.38) \times 16w} s',$$

while from the nitrogen observations we have—

$$LN = \frac{213.9^\circ}{99.59 \times 14w} s',$$

Hence—

$$\frac{LO}{LN} = \frac{597.9^\circ \times 99.59 \times 14}{213.9^\circ \times 239.10 \times 16} = 1.019.$$

This result confirms us in the view that the latent heat of oxygen is greater than that of nitrogen.

Similar ratios between the latent heats of hydrogen and oxygen and hydrogen and nitrogen are of importance in themselves, having regard to future work, and even although the ranges of temperature may not be coincident,

nevertheless the change in the value of the specific heat of lead will not affect the ratios by much more than about 1 per cent, supposing we take the specific heat of lead to be the same in both.

Thus, taking two of the longest ranges for temperature, namely, hydrogen from 17° to -252.5° and oxygen from 17° to -182.5° , we get the ratio—

$$\frac{LH}{LO} = \frac{16 \times 79.58 \times 269.0^{\circ} \times 0.0291}{1 \times 710.78 \times 199.5^{\circ} \times 0.0295} = 2.38;$$

similarly, taking two short ranges, namely, hydrogen from liquid air and nitrogen from solid carbonic acid, we find—

$$\frac{LH}{LN} = \frac{14 \times 51.46 \times 64.5^{\circ} \times 0.0280}{1 \times 162.22 \times 117.5^{\circ} \times 0.0290} = 2.35.$$

From the former of these with $LO = 51.15$, we get $LH = 121.7$; and from the latter with $LN = 50.4$, we get $LH = 118.4$.

The latent heat of air is a quantity whose determination is of a different order from that of either oxygen or nitrogen, seeing that the liquid evaporated is not always of the same composition, and the composition has not always been noted. Behn made a determination of it, and found its value to be 50.8 grm.-calories (*Ann. d. Physik.*, 1900, IV., i., p. 271). But in dealing with this value later in his paper, he takes the composition of the liquid air employed as containing 93 per cent of oxygen. This result may therefore be more appropriately used as a lower limit to the latent heat of oxygen, and thus far as a corroboration of the present value found for oxygen. D'Arsonval states, without giving any details, that he found the latent heat of air to be 65 calories (*Comptes Rendus*, 1901, vol. cxxiii., p. 983). Shearer has examined this quantity carefully on two occasions, using the same method each time (*Phys. Rev.*, 1902, vol. xv., p. 191; 1903, vol. xvii., p. 472). He distinguishes clearly the effects of various compositions. In his earlier experiments he found that for air containing from 21.8 to 72 per cent of oxygen, the latent heat varied from 44.02 to 51.7 grm.-calories. In his later series, he found that for air containing from 48 to 90 per cent of oxygen, the latent heat rose from 50.6 to 59 grm.-calories. Still more recently Fenner and Richtmyer (*Phys. Rev.*, 1905, vol. xx., p. 81), employing Shearer's method, find that from about the composition of atmospheric air until the mixture contains about 94 per cent of oxygen (from their diagram) the latent heat remains apparently constant at 50.966 , and that then it appears to rise rapidly to 54.10 at 97.6 per cent of oxygen. They seem to accept 61 grm.-calories as the latent heat of oxygen, so that the increase from 97.6 per cent to 100 per cent is exceptionally rapid.

In the present series of observations, the liquid air employed was old, that is, it was very rich in oxygen. If therefore we take the density of the air in the gas-receiver as being equal to that of oxygen, we shall have values of the latent heat of liquid air erring by defect. In the earliest experiment the volume of gas given off was (at 0° , and 760 m.m.) 84.25 c.c. per grm. of lead, from 18.5° to -184.5° , whence—

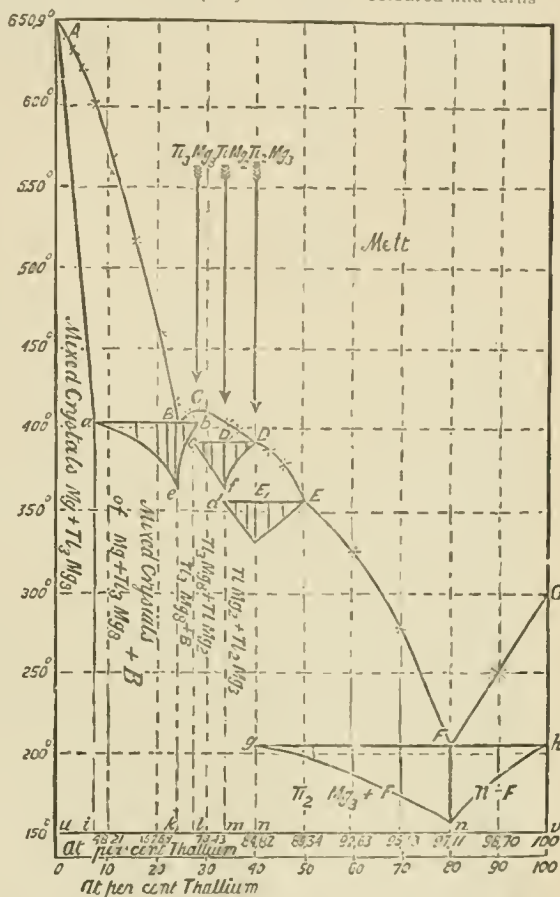
$$L_{air} = \frac{0.0295 \times 203^{\circ} \times 1000}{84.25 \times 1.43} = 49.7.$$

Similarly in a later case from 17.9° to -188° , the volume per grm. of lead was (at 0° and 760 m.m.) 79.34 c.c., whence $L_{air} = 53.41$. After this, several series of experiments were made in which a succession of half grms. of lead, 10 or 12 at a time, were dropped into old liquid air. In one experiment where 12 half grms. were employed, the mean volume of gas given off per grm. was (at 0° and 760 m.m.) 76.32 c.c., and the range of temperature was from 10.9° to -188° , thus giving the latent heat of air as 53.63 . These last values come very near those found by Fenner and Richtmyer; but the results are so varied that it is clear the question of the latent heat of air of very high oxygen concentration is one requiring further investigation.

MAGNESIUM-THALLIUM ALLOYS.

By GEORG GRUBB.

AN accurate investigation of the alloys of magnesium and thallium has not yet been performed. Carstanjen (*Journ. Prakt. Chem.*, 1867, cii., 84), for purely practical purposes, prepared an alloy with 50 per cent thallium and 50 per cent magnesium, in the hope of thus obtaining a material which would burn with an intensely green light, and would perhaps find technical application. It was found, however, that this alloy burnt with the colour of ordinary magnesium wire. As regards the properties of the alloy with 50 per cent thallium, he states that it is far less stable in air than pure magnesium, that it rapidly becomes discoloured and turns



grey, and then covered with moist caustic thallous oxide. Mellor (*CHEMICAL NEWS*, 1867, xv., 245) prepared alloys with 5, 10, 15, 25, and 50 per cent thallium, and makes the following statement concerning their properties:—"An alloy with 5 per cent thallium seems to make the magnesium less brittle and more ductile, but the alloys richer in thallium, e.g., those with 25 and 50 per cent thallium, are much more easily oxidised than pure magnesium."

Thus no information is to be found concerning the solidification points of the magnesium-thallium alloys, nor regarding the question whether in the series of the alloys chemical compounds of magnesium and thallium exist. The aim of this research is to examine the properties of the magnesium-thallium alloys on the basis of the method of thermal analysis.

The experimental arrangement of my earlier work was found suitable for determining the cooling curves. The

TABLE I.

Proportion of Tl in alloys.		Temperature of the breaks.	Eutectic crystallisation.							
Weight, per cent.	Atoms, per cent.		Temp.	Time.	Temp.	Time.	Temp.	Time.	Temp.	Time.
Melting-point of pure Mg, 650°; time of crystallisation, 125 secs.										
0	0		—	—	—	—	—	—	—	—
10.00	1.04	639.4°	—	—	—	—	—	—	—	—
20.00	2.90	632.1	—	—	—	—	—	—	—	—
30.00	4.87	623.7	—	—	—	—	—	—	—	—
40.00	7.38	600.2	—	—	—	—	—	—	—	—
50.00	10.66	577.6	402.4	23	—	—	—	—	—	—
60.00	15.18	519.3	401.0	37	—	—	—	—	—	—
70.00	21.78	477.1	404.2	85	—	—	—	—	—	—
72.50	23.94	417.1	405.9	120	—	—	—	—	—	—
73.64	25.00	408.8	405.7	55	—	—	—	—	—	—
75.00	26.37	411.3	403.2	15	—	—	—	—	—	—
76.06	27.50	Separation of Tl_3Mg_8 at 412.9°; time of crystallisation, 145 secs.								
77.50	29.13	412.3	—	—	393.2	25	—	—	—	—
78.78	30.70	411.2	—	—	393.0	60	—	—	—	—
80.73	33.33	405.0	—	—	392.9	100	—	—	—	—
82.50	36.00	399.5	—	—	392.4	30	355.2	35	—	—
83.70	38.00	395.9	—	—	392.9	20	355.6	60	—	—
84.82	40.00	389.8	—	—	—	—	355.5	85	—	—
86.10	42.50	386.9	—	—	—	—	355.4	60	—	—
87.50	45.52	377.8	—	—	—	—	355.4	40	205.2	10
90.00	51.79	353.7	—	—	—	—	—	—	204.6	25
92.63	60.00	325.3	—	—	—	—	—	—	205.2	60
95.00	69.40	278.4	—	—	—	—	—	—	205.6	105
97.11	80.00	—	—	—	—	—	—	—	205.2	155
98.70	90.00	251.3	—	—	—	—	—	—	205.3	65
100.00	100.00	Melting-point of pure Tl, 301.6°; time of crystallisation, 160 secs.								

breaks and critical-points of the curves were clearly shown. The oxidation of the alloys prepared in a current of hydrogen was exceedingly slight. By performing a few analyses it could be shown that the concentration of the alloys had not been appreciably displaced by burning. The thermo-element used to measure the temperature and the galvanometer were tested for constancy at the beginning and end of the investigation, by determining the melting-points of antimony, zinc, and lead. The temperature results of the cooling curves calculated on the scale of the air thermometer, as well as the times of crystallisation determined from them, are collected in Table I.

The table gives in the first column the proportion of thallium in the alloys in atoms and weight per cent. The second column gives the temperatures of the breaks; these are the temperatures at which the separation of a crystalline form begins. In the third column are the temperatures of the eutectics and their times of crystallisation in seconds. The temperatures can in all cases be determined correct to $\pm 1^\circ$, and the times of crystallisation to within ± 5 seconds. The concentrations of the alloys were weighed correct to 0.01 grm.

On the basis of the temperatures and times of crystallisation collected in Table I., the diagram of the magnesium-thallium alloys given in the figure was drawn. The concentrations, corresponding to the abscissæ, are expressed in atoms per cent, because then the diagram is clearer. The temperatures are represented by the ordinates.

The curve A, B, C, D, E, F, G represents the fusion-curve of the magnesium-thallium alloys; i.e., it connects with one another all the points at which the crystallisation of the crystalline form primarily separating begins. The eutectic horizontals are drawn through the points B, D, E, and F, and by dropping the perpendiculars proportional to the times in the usual way the eutectic curves are constructed.

The fusion-curve sinks from the melting-point of pure magnesium A in a curved line to the eutectic point B. The point B occurs at a concentration of 24 atoms per cent thallium and at a temperature of 403.7°.* From the point B the fusion-curve rises to the point C, from which it falls to the point D, at which the concentration amounts to 40 atoms per cent thallium. At C the fusion-curve has a

true maximum. Through the point D also a eutectic horizontal passes, the temperature amounting to 392.9°. From D the fusion-curve sinks further to E, through which the eutectic horizontal DE passes, which occurs at a temperature of 355.4°. The point E occurs at a concentration of 50 atoms per cent thallium. At E there is again a break in the curve. The curve then falls from E to its lowest point, F. From the point F the curve rises in a straight line to the melting-point of thallium, G. The point F occurs at a concentration of 80 atoms per cent thallium, at a temperature of 205.2°.

The examination of the fusion-curve shows us that a true maximum occurs on it at the point C, and two hidden maxima in the parts of the curve CD and DE. This shows the existence of three chemical compounds of magnesium and thallium.

In order to determine the formulæ of these compounds we applied the methods we have already described (*Zeit. Anorg. Chem.*, xlv., 123). Applying these methods first to the maximum C:—

1. The duration of the eutectic crystallisation at 403.7° becomes equal to zero at the point *b*, at 27.6 atoms per cent thallium, if we follow the course of the curve *eb*; the duration of the eutectic crystallisation at 392.9° becomes zero at 27.3 atoms per cent thallium, as shown by the course of the curve *cf*. The mean of these two values is 27.45 atoms per cent thallium.

2. By graphic interpolation from the observed points of the fusion-curve, the maximum was found at about 27.4 atoms per cent thallium.

3. The alloy with 27.50 atoms per cent thallium has the cooling curve of a pure substance, with a time of crystallisation of 145 seconds. The critical-point lies higher than the temperature of the beginning of crystallisation in the neighbouring alloys.

The formulæ to be considered for the compound at the maximum C are Tl_2Mg_5 with 26.37, Tl_3Mg_7 with 30.00, and Tl_3Mg_8 with 27.26 atoms per cent thallium. The mean value established by the above three methods for the concentration of the compound amounts to 27.45 atoms per cent thallium. The formula Tl_3Mg_8 is closest to this value. In order to determine whether the concentration of the maximum had been somewhat displaced by burning, three alloys from the concentration region in question were analysed, the magnesium being weighed as pyrophosphate

* For the eutectic temperatures in the diagram the mean values are taken from the eutectic temperatures given in Table I.

and the thallium as thallos iodide. Each analysis was repeated. The results are given in Table II.

TABLE II.

Weighed composition in atoms per cent.		Determined by analysis. Atoms per cent.	
Tl.	Mg.	Tl.	Mg.
26.37	73.63	26.46	73.49
		26.55	73.65
27.50	72.50	27.56	72.39
		27.59	72.46
29.13	70.87	29.20	70.74
		29.11	70.90

The values found analytically agree to within 0.1 per cent with the concentration of the maximum calculated from the weighed quantities; hence the concentration of the maximum of the fusion-curve is proved to be 27.35 atoms per cent thallium with a possible error of ± 0.1 per cent. We are thus forced to accept the formula Tl_3Mg_3 for the compound crystallising out at the maximum c.

To determine the formulæ of the compounds formed at the eutectic temperatures D and E, we proceed as follows:—

1. The duration of crystallisation at the temperature of the straight line *c d* has a maximum at the point *D*, at a concentration of 33.33 atoms per cent thallium.

2. The duration of crystallisation on the straight line *c d* becomes zero at the point *d*, with a percentage of thallium = 33.4 atoms per cent.

The concentration of 33.33 atoms per cent thallium corresponds to the formula $TlMg_2$. The agreement of the values given under 1 and 2 for the composition of the compound proves the correctness of the formula $TlMg_2$.

In the same way we determine the composition of the compound formed at the temperature of the horizontal *E*:—

1. The duration of crystallisation at the temperature of the straight line *d E* has its greatest value at a concentration of 40.00 atoms per cent thallium.

2. The duration of eutectic crystallisation at the temperature of the straight line *g h* becomes equal to zero at the point *g*, at a concentration of 40.2 atoms per cent thallium.

The formula Tl_2Mg_3 corresponds to a concentration of 40 atoms per cent thallium, and we must therefore accept it for the compound crystallising at the point *E*.

The compound Tl_3Mg_3 melts to a homogeneous liquid, because a maximum occurs on the fusion-curve at the composition of this compound. The two other compounds, $TlMg_2$ and Tl_2Mg_3 , when they melt, split up into crystals of different composition and melts, the compound $TlMg_2$ decomposing at 392.9° according to the equation—

$TlMg_2 \rightleftharpoons 0.0796 Tl_3Mg_3 + \text{melt } (0.9204 Tl + 1.9204 Mg)$, while the compound Tl_2Mg_3 is decomposed at 355.4° according to the following equation:—

$Tl_2Mg_3 \rightleftharpoons 0.1194 TlMg_2 + \text{melt } (1.8806 Tl + 2.8806 Mg)$.

It now remains to be decided whether pure magnesium crystallises from the melt which is poor in thallium, and pure thallium from the melt which is rich in thallium. The duration of crystallisation at the temperature of the eutectic horizontal, *h g*, becomes equal to zero at the concentration of pure thallium. There is therefore no reason for assuming the existence of mixed crystals in the concentration region below the line *F G*. This question was not investigated further microscopically, because such an examination is rendered very difficult owing to the great variability of, and the difficulty of polishing, the soft conglomerate. The duration of eutectic crystallisation at a temperature of 403.7° becomes equal to zero at 7 atoms per cent thallium, as may be seen from the diagram. We are therefore compelled to assume that from the melts rich in magnesium, pure magnesium does not crystallise out, but a series of mixed crystals, the last member of which contains 7 per cent thallium. The concentration of the saturated

mixed crystals of this series may be determined by extrapolation of the eutectic times on the straight line *a b*.

The microscopic examination of the polished surfaces of alloys between 0 and 7 atoms per cent thallium must thus reveal a perfectly homogeneous structure; it is supposed that the rate of cooling of the alloys is so slow that the exchange between melt and primarily separated crystals can take place completely. The examination of the polished surfaces gave the following results:—Those of alloys with 1.04 and 2.90 atoms per cent thallium had a perfectly homogeneous structure. A specimen with 4.87 atoms per cent thallium, however, still contained some eutectic, *B*. But by keeping the temperature of this alloy for about half-an-hour between 440° and 405°, the eutectic might be almost completely removed.

The following remarks may be made concerning the fields of the diagram:—Above the curve *A, B, C, D, E, F, G* all alloys are liquid. In the fields bounded by the fusion-curve and the eutectic horizontal there is always a crystalline form in equilibrium with melt. Below the eutectic horizontals, thus below the line *A a*, the alloys are perfectly solidified. The fields are compared in Table III.

TABLE III.—Fields.

I. Liquid Region:—Limited on the lower side by the fusion-curve *A, B, C, D, E, F, G*.

II. Region with one crystalline form:—

<i>A u i a</i> ..	Mixed crystals of $Mg + Tl_3Mg_3$.
<i>A b a</i> ..	Mg .
<i>C b b</i> ..	Tl_3Mg_3
<i>C d c</i> ..	Tl_3Mg_3
<i>D i D e d</i> ..	$TlMg_2$ + melt.
<i>E i E f g</i> ..	Tl_2Mg_3
<i>F g h</i> ..	Tl

III. Region with two crystalline forms:—

<i>a b k i</i> ..	Mixed crystals of $Mg + Tl_3Mg_3$ + eutectic ($Mg + Tl_3Mg_3$).
<i>B b l k</i> ..	Tl_3Mg_3 + eutectic ($Mg + Tl_3Mg_3$).
<i>c D i m l</i> ..	$Tl_3Mg_3 + TlMg_2$.
<i>d E i w m</i> ..	$TlMg_2 + Tl_2Mg_3$.
<i>g f n w</i> ..	Tl_2Mg_3 + eutectic ($Tl + Tl_2Mg_3$).
<i>F h v n</i> ..	Tl + eutectic ($Tl + Tl_2Mg_3$).

A microscopic examination of the alloys was then performed in order to prove the results obtained from the fusion diagram. The polished specimens with 0 to 7 atoms per cent thallium have already been described. The alloys between 7 and 24 atoms per cent thallium must consist of saturated mixed crystals with 7 atoms per cent thallium, surrounded by eutectic *B*. The eutectic *B* is composed of small saturated mixed crystals and small crystals of the compound Tl_3Mg_3 . The photograph, magnified sixty times, of a polished surface with 15.18 atoms per cent thallium, etched by standing in the air, shows primarily formed branching white mixed crystals, surrounded by blackened eutectic *B*, the constituents of which cannot be recognised, because they blacken instantly in the air. Between 24.00 and 27.26 atoms per cent thallium, primarily separated crystals of the compound Tl_3Mg_3 must exist, surrounded by eutectic *B*. The photograph, magnified fifty times, of a polished surface with 26.37 atoms per cent thallium, etched by allowing to stand in air for a short time, shows clearly the blackened primarily separated crystals of the compound Tl_3Mg_3 surrounded by eutectic *B*. As the surface was exposed to the air only for a very short time, the constituents of the eutectic can still be recognised.

The alloys between 27.26 and 33.33 atoms per cent thallium should, according to the diagram, contain the compounds Tl_3Mg_3 and $TlMg_2$. The photograph of a polished surface with 29.13 atoms per cent thallium shows white crystals of the compound $TlMg_2$ surrounded by the compound Tl_3Mg_3 . As we are now in the immediate neighbourhood of the maximum *c*, the quantity of the compound Tl_3Mg_3 is very large, and the secondarily formed

crystals of TiMg_2 are therefore embedded in the compound Ti_3Mg_8 .

The alloys between 33.33 and 40.00 atoms per cent thallium consist of primarily formed compound TiMg_2 and secondarily separated compound Ti_2Mg_3 . The photograph of a polished surface with 36.00 atoms per cent thallium, which is etched by standing a long time in air, shows the primarily separated clear crystals of the compound TiMg_2 arranged in lines; they are surrounded by the compound Ti_2Mg_3 , which very rapidly blackens in air owing to oxidation.

It is very difficult to photograph the polished surfaces of alloys which contain the primarily formed compound Ti_2Mg_3 because of the extraordinarily rapid oxidation of the compound in air. When freshly prepared it consists of fairly long silvery white crystalline needles, which, however, are exceedingly unstable in air. Photographs of a polished surface with 45.52 atoms per cent thallium show these white needles of the compound Ti_2Mg_3 strongly attacked by oxidation, surrounded by a black mass, which consists partly of oxidised compound and partly of the eutectic F .

As has been repeatedly mentioned before, the thallium-magnesium alloys are blackened by oxidation in the air. In damp air they are attacked more rapidly than in dry air. Of the three thallium-magnesium compounds, Ti_2Mg_3 is oxidised most quickly and Ti_3Mg_8 rather more slowly, while TiMg_2 is the most stable. The difference of the stability of the three compounds is, however, not great.

In conclusion I wish to express my hearty thanks to Professor Tammann for suggesting this work to me, and for his kind advice and assistance.—*Zeit. Anorg. Chem.*, xlvii., 84.

ALTERNATE CURRENT ELECTROLYSIS.*

By ERNEST WILSON, M.I.E.E.,
Professor of Electrical Engineering, King's College, London.

IT is well known that if an alternate current be passed between metal electrodes in an electrolyte, electrolysis may take place. For instance, it has been shown that, in the case of lead plates in dilute H_2SO_4 the SO_4 combines with the lead to form PbSO_4 , and the plates are eaten away. The present paper gives an account of some experiments made to determine what may be the effect upon certain metals of passing alternating currents between them and certain electrolytes under given conditions. Suppose that an alternating current be passed between electrodes in an electrolyte, and that the curves of potential difference between the electrolyte and one electrode and the curve of current be observed. Let the curve of potential difference be corrected for the fall of potential due to the conductivity of the electrolyte, thereby giving the E.M.F. of electrolysis measurable in volts. Let the current curve be integrated, giving the quantity of electricity measurable in coulombs. We should expect that as the maximum coulombs per half period increased, the E.M.F. of electrolysis would also increase until it had the value given by continuous current, and that with further increase of the maximum coulombs per half period the E.M.F. of electrolysis would have a constant amplitude. If the process were truly reversible, we should expect to find that the E.M.F. of electrolysis and current would have an effective phase displacement of one quarter period in time.

The plates in a given cell were of like metal, and were separated $\frac{1}{8}$ inch (0.317 c.m.), with their opposing faces parallel. They were held in position by wooden blocks and ebonite distance pieces bolts and nuts. The wooden pieces covered the back of each plate, with the view of confining the current to the opposing faces. The area of each of the surfaces exposed in the electrolyte was about 150 sq. c.m., but not all of each plate was submerged. For the purpose of obtaining the potential difference

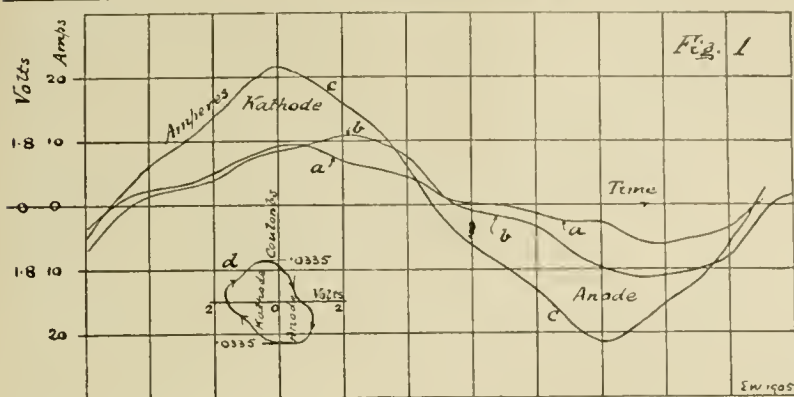
between the electrolyte and one of the plates, an exploring electrode, cut from the plate itself, was placed in the electrolyte midway between the plates, and by the aid of a revolving contact-maker on the alternator shaft and a quadrant electrometer the curve was obtained. The distance between the exploring electrode and the plate was about 1 m.m. Similarly the curve of current was obtained by observing the instantaneous value of the potential difference across a non-inductive resistance placed in the circuit. The curve of current was controlled by inserting a considerable non-inductive resistance in the circuit. The E.M.F. of electrolysis is therefore a dependant variable as regards wave-form. Further research should deal with variation of wave-form. Small test pieces were placed in the solution to see if any action took place without the passage of the electric current. It should be noted that during the experiment the solution in a given cell changes, and therefore an average result has been obtained. No special care was taken to keep the temperature of a given cell constant, and the volume of fluid in each cell was about 2 litres.

Lead.

H_2SO_4 dil.—The electrolysis produced by an alternating current (when passed between lead electrodes in dilute H_2SO_4 (100 pts. H_2O + 5 pts. H_2SO_4 by vol.) has already been studied (see *The Electrician*, April 18, 1902). It was shown that for a given R.M.S. current density over the plate, less lead per sq. cm. per hour was dissolved at frequency 92.5 than at frequency 21.5. A R.M.S. density of 0.0236 ampère per sq. c.m. would eat away the lead in one year to a depth of 2.6 c.m. and 4.8 c.m. respectively at the above frequencies. The same current density with direct current would eat away 70 c.m. in a year. Since the R.M.S. current density is the same and the wave-form is the same in the two experiments, the maximum coulombs per half period will vary in the inverse ratio of the frequencies, but we do not find that the dissolved lead varies as the maximum coulombs. Referring to the table, Experiments 1 and 2 show that at frequency 21.5, 0.00629 grm. per hour per sq. c.m. were dissolved. This multiplied by the ratio of the frequencies would give 0.00146 grm. per hour per sq. c.m., as against 0.00344 actually measured. Experiment 3 was undertaken to discover if at 92 frequency and approximately the same maximum coulombs per half period, the weight of dissolved lead would be the same as in Experiment 1. We find that five times as much lead is dissolved at the higher R.M.S. current density. The effect may depend upon the current density, since the maximum coulombs per half period are slightly less in Experiment 3 than in Experiment 1, whereas the current density is nearly four-fold. Also in Experiment 3 the density of the electrolyte fell to 1036 in eight hours, as against 1049 in fifteen hours in Experiment 1.

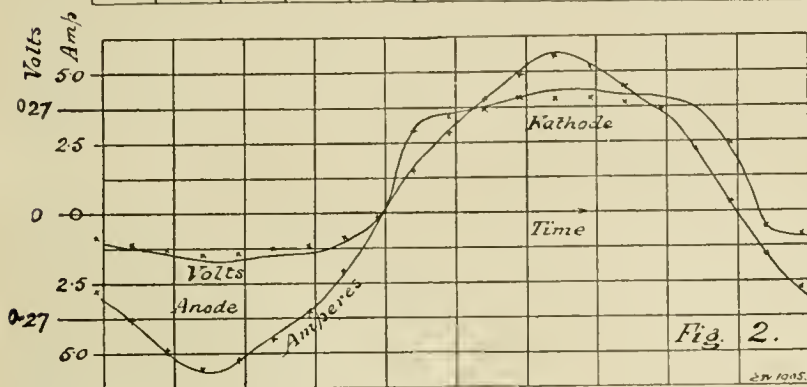
In Experiment 3, curve *a* Fig. 1 is the potential difference between the lead exploring electrode and one plate. This can also be taken to give the E.M.F. of electrolysis, since the conductivity drop is sufficiently small. The curve *b* is the potential difference between the plates, and *c* is the curve of current. It will be observed that the E.M.F. of electrolysis *a* does not change sign at the moment the plate begins to be an anode; the difference in phase represents the time taken to reverse the E.M.F. existing since the coulombs were last a maximum. The work done during this time is returned to the system. This is not the case when the plate begins to be a kathode, as the reversal of E.M.F. occurs simultaneously with the current. The coulombs have been plotted co-ordinately with the E.M.F. of electrolysis, giving the cyclical curve *d*. As was previously pointed out, more work is done on the system during the time that the plate is a kathode than when it is an anode. The evolved hydrogen combines with the oxygen of the PbO_2 , leading to the formation of PbSO_4 , the maximum coulombs being sufficiently great to produce the peroxide. The plates are not, however, fully polarised in this experiment, much less so in Experiment 2, and it may be that the low result in Experiment 2 is attributable

* A Paper read before the Faraday Society. July 3, 1905.



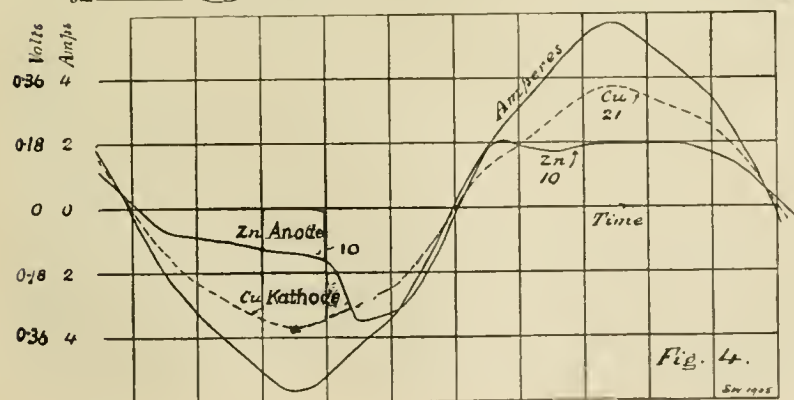
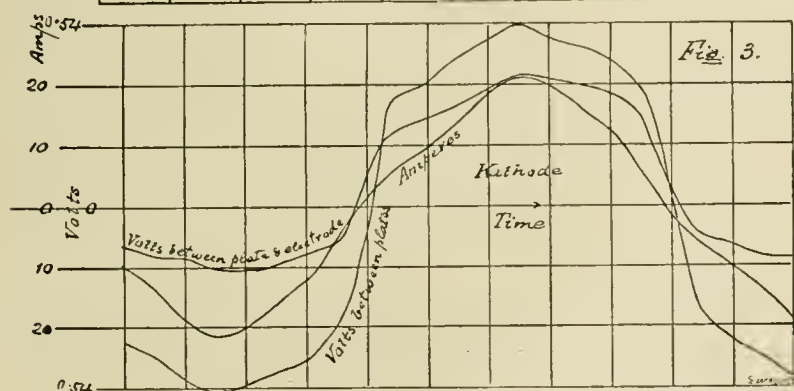
to the small value of the maximum coulombs. The electrolysis with lead electrodes at low current density is a subject worthy of further research.

It is conceivable that electrolysis by alternating currents may be influenced by diffusion and certain local conditions. When observing the E.M.F. of electrolysis it was noticed that the electrometer deflection became unsteady at certain times of a period, indicating how easily it may be affected. In these experiments the plates were purposely placed near together, and did not give such facilities for diffusion as might otherwise have been obtained.



Zinc.

H_2SO_4 dilute. — The most marked effects with zinc have been obtained when it has been amalgamated and placed in dilute H_2SO_4 (100 pts. H_2O + 5 pts. H_2SO_4 by vol.). In Experiments 4 and 5 the current densities are nearly the same, but the frequencies are different. The dissolved zinc at the higher frequency is greater than we should expect if we simply took the ratio of the maximum coulombs per half period into account. The figures are 0.00147, as against 0.00189 observed, and agree more closely than was the case in Experiments 1 and 2. Again comparing the results of Experiments 4 and 6, in which the maximum coulombs are the same, we find 0.0053 grm. per sq. c.m. per hour dissolved, as against 0.00695 at the higher frequency. It should here be noted that in Experiment 6 the plates were not freshly amalgamated, nor was the solution freshly put up. After weighing at the close of Experiment 5, the plates were again placed in the same solution, and Experiment 6 made. In Experiment 7 freshly amalgamated plates and fresh solution were used, and the result is quite different from that obtained in Experiment 6. To test the importance of the degree of amalgamation and the period of rest between amalgamation and starting the experiment, four new zinc plates were amalgamated to the same degree as nearly as possible, and left nearly three days before being used. Experiments 8 and 9 were then made. Comparing Experiment 9 with 7, in which the duration of test, frequency, and current density were the same, the agreement is better, since the average grms. per sq. c.m. per hour are



respectively 0.00103 and 0.00166. The results no doubt depend upon the preparation of the plates before the experiment.

The full line curves in Fig. 2 were obtained during Experiment 4, and the crosses show the corresponding points obtained during Experiment 5. The agreement as to wave-form, phase, and amplitude of the E.M.F. of electrolysis at the two frequencies demonstrates that in the case of amalgamated zinc in dilute H_2SO_4 a change from 25 to 92 periods per second does not affect the possibility of the E.M.F. of electrolysis taking the same wave-form, amplitude, and phase relation. Experiments made with sufficiently increased frequency might throw some light upon the time taken to accomplish dissociation. Fig. 3 shows the curves obtained during Experiment 7. The phase relations are practically the same, but the effect of conductivity upon the E.M.F. observed between the exploring zinc electrode and one plate when the current is near a maximum, is slightly observable. Test pieces of amalgamated zinc were in the solutions during the experiments, and were practically unchanged in weight.

Zinc Chloride (strong).—The zinc plates in Experiment 10 had, when immersed in the solution, a smooth clean surface, and when taken out after the test they were highly oxidised. In Fig. 4, curve 10 was obtained between the zinc exploring electrode and one plate. The potential difference rises to a maximum of 0.32 volt when the plate is an anode, of which 0.01 volt may be due to conductivity. Curve 10 may be taken to be the E.M.F. of electrolysis, and it is nearly in phase with the current. Although the plates have increased in weight during the experiment, it is due to oxidation which leads to their disintegration.

Zinc Sulphate (saturated).—Experiment 11 has had little or no effect upon the zinc plates immersed in saturated zinc sulphate solution. The potential difference between the zinc exploring electrode and one plate has the same wave-form as, and is in phase with, the current. There is no visible oxidation, and the process is probably almost reversible.

Sodium Sulphate (strong).—Under the conditions of Experiment 12 the zinc plates immersed in this solution have gained in weight, and are still heavier (than before experiment) after being rubbed with wash-leather to remove the surface oxide. The potential difference between the exploring electrode and one plate is shown in Fig. 5, curve 12.

(To be continued).

CORRESPONDENCE.

INSTITUTE OF CHEMISTRY EXAMINATIONS.

To the Editor of the Chemical News.

SIR,—In connection with the subject raised by your correspondent "Technicus" in the CHEMICAL NEWS (vol. xcii., p. 168), I should be very pleased if you would insert the following:—

"Technicus" remarks:—"There are many chemists employed in technological work who have never had the opportunities and advantages which are necessary to become A.I.C. or F.I.C." This raises the question: Why have not the Institute of Chemistry inaugurated examinations for a degree for technical chemists (A.I.T.C. or F.I.T.C.)?

Young chemists employed in iron and steel works, and other laboratories in connection with manufacturing processes, have not the time to study for such examinations as are required to obtain the A.I.C. degree, much less the qualification required—of working under an Associate or Fellow. In order to get the degree, they must proceed in a roundabout way—by qualifying for the B.Sc. degree. This means years of hard work, employing every moment of their spare time, and allowing no time for recreation and fresh air, which those who work in a large ironworks

laboratory will agree is very much a necessity to them. This being the case, why does not the Institute of Chemistry draw up a scheme of examination bringing in those subjects necessary to a technical or metallurgical chemist?

Taking as an example the case of a metallurgical chemist, let me suggest a scheme which would prove useful and suitable for him.

Preliminary Examination.—(a). Elementary Inorganic Chemistry, theoretical and practical. (b). Elementary Iron and Steel Manufacture. (Paper set being similar to City and Guilds examination questions). (c). Practical Metallurgy, elementary. (d). First and Second Stage Mathematics. (e). One of following three subjects:—(1) Elementary Machine Construction and Design, (2) French, (3) German.

Students having already passed Board of Education or City and Guilds of London examinations in any of these subjects, elementary or advanced stages, to be exempted from examination on producing certificates.

Intermediate Examination (no exemption).—(a). Advanced Inorganic Chemistry, theoretical and practical. (b). Elementary Theoretical Organic Chemistry. (c). Advanced Iron and Steel Manufacture. (d). Advanced Practical Metallurgy. (e). Third Stage Mathematics. (f). Two of following three subjects:—(1) Advanced Machine Construction and Design, (2) French, (3) German.

Final Examination.—(a). Analytical Chemistry (this paper to cover the whole of practical work necessary to a first-class chemist, and including questions on the theory of such analysis). (b). Honours Iron and Steel Manufacture. (c). Honours Practical Metallurgy. (d). Fourth Stage Mathematics. (e). French. (f). German.

A scheme of this description would be within reach of any technical chemist with any ambition at all, and would cover the work necessary to him and be at the same time sufficiently difficult to ensure only the really competent ones obtaining the degree. For chemists other than metallurgical, the Iron and Steel and Practical Metallurgy could be replaced by subjects dealing with their special line.

I feel sure that all technical chemists will agree with me that such a scheme as I have here proposed would be beneficial, and ought to be carefully considered by the Institute of Chemistry or some other similar body; and if the Institute have the interests of chemistry at heart, they should not longer delay in such an important matter.

Hoping that this letter may be the means of bringing about the inauguration of some such degree, I am, &c.,

ONE OF MANY.

CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 14, October 2, 1905.

Isostrychnine.—A. Bacovesco and Amé Picet.—When strychnine is heated with water in sealed tubes to a temperature of 160—180°, it slowly dissolves, and, on cooling, the solution deposits long prismatic needles which fuse at 214.5°. An analysis of this substance shows it to have the formula $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2 + 3\text{H}_2\text{O}$. It is therefore an isomer of strychnine, and is called by the authors *isostrychnine*. Under the action of sodium ethylate this substance is transformed entirely into isostrychnic acid. It can therefore be considered as an anhydride of this acid, in the same way as strychnine is of strychnic acid. The isomerism of the two bases is consequently of the same nature as that of the two acids.

Berichte der Deutschen Chemischen Gesellschaft.

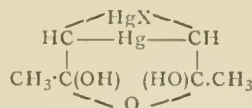
Vol. xxxviii., No. 12, 1905.

Action of Nitrogen upon Water-vapour.—O. F. Tower.—It has been shown that at high temperatures nitrogen and water-vapour react to a very slight extent according to the equation $N_2 + 2H_2O = 2NO + 2H_2$. The author has now performed experiments to find out whether nitric oxide is formed in measurable quantities, and whether it is accompanied by the equivalent quantities of hydrogen. The nitrogen was generated from ammonium sulphate and potassium nitrite, and purified by passing through sulphuric acid and over ignited copper. The exit gases were tested for nitric oxide by mixing them with oxygen in order to convert the nitric oxide into the dioxide, and the latter was then absorbed in a Winkler's gas burette with 85 per cent sulphuric acid. The acid was shaken up with mercury in a Lunge's nitrometer, and the volume of the nitrogen dioxide read off. In the first experiments, although the temperature amounted to about 2000°, only traces of nitric oxide were found. If sparks were passed through the mixed gases appreciable quantities of nitric oxide were formed. In these experiments the hydrogen set free was determined, and it was found that hydrogen and nitric oxide are formed in equivalent quantities according to the above equation. To obtain equilibrium between nitrogen and water-vapour an electrically heated iridium furnace was used. It was found that the action between nitrogen and water at high temperatures can be increased to any extent by increasing the partial pressure of the nitrogen.

Perchromates.—K. A. Hofman and H. Hiendlmaier.—In preparing ammonium diperchromate from chromium hydroxide or ammonium chromate and hydrogen peroxide in presence of ammonia, the authors find that the amount of ammonia present has a decided influence upon the reaction. If the solution contains either no free ammonia or else ammonia in large excess, crystallised stable products are obtained. It was found that chromic acid mixed with one molecule of hydrogen peroxide in 10 to 20 per cent ammoniacal solution gives no salt, but unites with three ammonia molecules to form the compound $CrO_4(NH_3)_3$, which is capable of existing in two forms, the second or β -form being produced when the concentration of the ammonia is the highest possible. Investigation of the perchromate shows that it is not a salt, but an amine. For, according to the results of the elementary analysis and of the oxygen determinations, only 9 hydrogen atoms are present to 3 nitrogen atoms, while 3 ammonium groups would require 12 hydrogen atoms. This of course could be explained by supposing that 2 ammonium groups and 1 amido group are present, but this supposition has been disproved by Wiede. The α - and β -forms behave very similarly, both qualitatively and quantitatively, towards alkalis and acids. To prove that these products are not salts but amines, the action of acetic acid upon them was investigated. It was then found that the three NH_3 molecules of the peroxide $CrO_4(NH_3)_3$ are not attacked by strong acetic acid. When it is remembered that both secondary potassium chromate and secondary ammonium chromate give up at least half their alkali with dilute acetic acid, this appears to prove that the peroxide contains no ammonium, but amine groups. If ammonium bichromate solution, ammonium nitrate, and hydrogen peroxide are mixed in the cold, ammonium perchromate, $NH_4CrO_5 + H_2O_2$, is formed; this has already been prepared by Wiede.

Compounds of Ketones and Aldehydes with Mercury Oxide.—S. M. Auld and A. Hantzsch.—The compound formed by dissolving mercuric oxide in an alkaline aqueous acetone solution is characterised by its solubility in water. It has never been thoroughly investigated, because it readily passes into an amorphous form insoluble in water, having the empirical formula $2C_3H_5O \cdot 3HgO$. If the soluble form is rapidly freed from hydroxyl ions, it is fairly stable and yields well characterised haloid salts. With haloid acids it gives mercuric salts of the formula

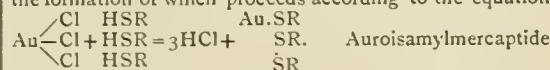
$C_6H_{10}Hg_3O_3X_2$, and therefore contains two hydroxyl groups combined with Hg : $C_6H_{10}HgO(HgOI)_2$. With bromine it yields asymmetric dibromacetone, $CH_3 \cdot CO \cdot CHBr_2$, and is therefore a derivative of asymmetric dimeric acetone, $CH_3CO \cdot CH(HgOI)_2$. Finally, it is indifferent towards hydroxylamine and phenylhydrazine, and hence contains no intact ketone carbonyles. Thus the compound is probably trimeric mercuric diacetone hydrate, and the structural formula is—



Grignard's Reaction.—Adolf Baeyer.—It is generally necessary when acting with magnesium on benzene bromide or iodide and analogous compounds to render the magnesium active by the addition of some iodine, in order to enable it to act upon the organic compound. With bromine or iodine alkyl, magnesium acts at once in ethereal solution. The author has now found that magnesium becomes capable of acting on the benzene derivatives without the addition of iodine or alkyl compound, if the finely divided metal is previously coated with a thin layer of magnesium iodide. The magnesium thus treated forms a dull grey powder, which becomes brown in time, and must be carefully protected from moisture. This active magnesium gives off a gas with water. With methyl alcohol gas is evolved energetically, until all the magnesium is dissolved, and a white mass, probably consisting of magnesium methylate, is left behind. Ethyl alcohol acts less energetically, and amyl alcohol not at all. The active magnesium has no action upon benzene chloride, but reacts very violently with benzene bromide. It also reacts with all iodated anilines and dimethyl anilines, most energetically with the ortho- and least with the para-compounds.

Cellulose.—H. Riesenfeld and F. Taurke.—The best solvent for cellulose is a solution of copper oxide in ammonia, but the authors found that a specimen of pure cellulose was quite insoluble in this reagent. On the other hand, a solution of copper carbonate in ammonia was found to be a very good solvent (prepared by adding the calculated quantity of sodium carbonate to an aqueous solution of copper sulphate, filtering off the green precipitate, washing and dissolving in concentrated ammonia). The cellulose dissolved by this reagent is precipitated by salts, acids, water, and alcohol. Iron, nickel, and tin have no effect upon the solution, while zinc, cadmium, aluminium, and lead precipitate both copper and cellulose. When the solution is heated, a brown precipitate separates. This was dried and analysed, and it was found that on treatment with dilute acid the copper goes into solution, and the cellulose remains behind quantitatively. Analysis shows that the percentage of copper present in the precipitate is nearly constant, while the percentage of cellulose varies somewhat, possibly owing to difficulties attendant upon the drying process. It is decomposed by acids and is soluble in ammonia.

Compounds of Gold with Organic Radicles containing Sulphur.—F. Herrmann.—The author has investigated the properties and preparation of auromercaptide, the formation of which proceeds according to the equation



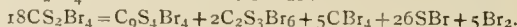
and aurobenzylmercaptide are prepared similarly. With dibenzyl sulphide gold chloride forms colourless crystalline needles. Under no circumstances is a compound yielded which contains more than one molecule of sulphur to an atom of gold. The compound has the composition $\text{AuS}(C_7H_7)_2 \cdot \text{Cl}$. It is difficultly soluble in ether and cold alcohol, easily soluble in boiling alcohol, and almost insoluble in carbon tetrachloride. The best solvent is chloroform. The compound is dimorphic. From hot super-saturated solutions, or if it is precipitated from its solution

by the addition of indifferent reagents, it separates out on cooling in the form of needles, while on slow evaporation of solutions at ordinary temperatures large rhombohedral-looking crystals are obtained. Both modifications behave similarly on heating—they melt at 122° , metallic gold being split off. The compound is not very stable; it can hardly be re-crystallised without giving off ammonia. In all reactions it behaves as an aurous compound, and its constitution appears to be shown by the formula $\text{Cl.Au:S}(\text{C}_7\text{H}_7)_2$ or $\text{Au:S}(\text{C}_7\text{H}_7)_2\text{.Cl}$. With aqueous ammonia and ether it dissolves rapidly, forming two layers. The upper one, on evaporating off the ether, leaves pure dibenzyl sulphide. If the aqueous layer is filtered and evaporated over sulphuric acid, as the ammonia gas escapes white spheroidal microcrystalline concretions separate off at the surface of the liquid, and these finally form a layer all over the liquid, so that the evaporation of the water is stopped until the layer is broken through. Finally, a chalky crust is left behind, appearing slate-grey on the surface. The composition corresponds approximately to that of auroamine chloride, $\text{Au.NH}_3\text{.Cl}$. A compound $\text{AuCl}_2\text{S}(\text{C}_7\text{H}_7)_2$, dichlorauridibenzyl sulphide, is prepared by mixing ethereal solutions of two molecules of gold hydrochloride and three molecules of dibenzyl sulphide. It is an auric compound, and with alcoholic ammonia solution yields a precipitate which, when dry, explodes slightly on heating.

Decomposition of Casein by Ozone.—C. Harries.—Casein was dissolved in $\frac{1}{10}$ N caustic soda and exposed to the action of ozone until dilute hydrochloric acid gave no precipitate of unchanged casein. The solution thus obtained contained no hydrogen peroxide, and only feebly reduced Fehling's solution. After standing, the ozonised solution developed a characteristic smell of melted sugar. The author then endeavoured to isolate the sugar substance by means of phenylhydrazine. An osazone was thus formed, which contained almost all the phosphorus of the casein, and possessed acid properties, reduced Fehling's solution, like the osazone of milk-sugar, but was difficultly soluble in water. When the ozonised solution was treated with lead acetate, a white precipitate resulted, from which, on treatment with sulphuretted hydrogen, a white substance soluble in water could be obtained, containing nearly 2 per cent phosphorus, and over 40 per cent oxygen, while the nitrogen amounted to 5 to 7 per cent. The substance had an acid reaction, gave no biuret reaction, and no precipitate with phosphorus tungstic acid. When its neutralised aqueous solution was warmed with phenylhydrazine hydrochloride and sodium acetate, and normal hydrochloric acid was added, the same yellow osazone was obtained as was produced directly from the ozonised liquid.

Action of Sulphur on Carbon Tetrabromide.—A. von Bartsch.—An intimate mixture of one molecule of dry carbon tetrabromide with two molecules of flowers of sulphur was heated in a fractionating flask on an oil-bath, and the products were collected in a cooled vessel. The mixture melted at 100° – 110° , and a reaction began to occur at 150° – 160° . At 180° – 195° a liquid (first yellow and then dark red) distilled over. The residue in the flask was dark blue. This was purified by shaking with ether and heating with alcohol, and dried at 100° . The blue product was insoluble in most solvents, with the exception of fused phenol, with which it readily gave a blue solution. It dissolved in hot concentrated sulphuric acid very readily, and fairly easily in concentrated nitric acid and hydrochloric acid. Aniline appeared to act upon it chemically. Analysis showed that the composition is $\text{C}_6\text{Br}_4\text{S}_4$. Probably the compound belongs to the aromatic series, in which case the sulphur forms the chromophore group .S.S., and the compound is thus chromogenic. The distillate was then examined. It was heated on a water-bath, when more than half distilled over, giving a liquid which is not a single compound, but probably a mixture of free bromine and carbon disulphide, containing also small quantities of bromine. From the residue in the boiling flask an oil could be extracted from

which a crystalline mass of carbothiohexabromide, $\text{C}_2\text{S}_3\text{Br}_6$, could be separated. Thus the products of the action of sulphur on carbon tetrabromide are the blue compound $\text{C}_6\text{S}_4\text{Br}_4$, the white crystalline compound $\text{C}_2\text{S}_3\text{Br}_6$, carbon tetrabromide, carbon disulphide, and bromine, and also, according to all indications, large quantities of bromine sulphide. Probably first of all CS_2 and Br are formed, which partly go over as such, and partly combine to CS_2Br_4 . This then reacts thus:—



The tetrabromide is partly decomposed to bromine, bromine sulphide, and carbon, which latter is contained in the blue residue. The carbothiohexabromide and carbon tetrabromide dissolve in the bromine sulphide or bromine, and go over at a relatively low temperature. If the bromine is distilled off the liquid boils at a higher temperature, at about the boiling-point of bromine sulphide. This liquid dissolves in ether, from which the carbothiohexabromide may be precipitated by alcohol, and the carbon tetrabromide by water in the filtrate.

Preparation of Perchloroethane.—K. A. Hofmann and E. Seiler.—The authors have found that aluminium amalgamated superficially, when treated with carbon tetrachloride at 70° , yields aluminium chloride, considerable heat being evolved, and large quantities of hexachloroethane are simultaneously formed. To avoid loss of material the reaction is allowed to proceed to its termination, the brown liquid is poured off and mixed with twice its volume of ice-water. The excess of carbon tetrachloride is then distilled off. At 100° the perchloroethane begins to go over with the water-vapour. By shaking with ether the perchloroethane is separated from the water, and it is dried and evaporated *in vacuo*. The preparation has the characteristic camphor smell, rhombic crystalline form, and sublimation-point of pure perchloroethane, and the authors also determined its percentage of chlorine, which agrees with that of C_2Cl_6 . With chloroform amalgamated aluminium reacts in such a way as to form carbon, even if the chloroform is present in excess. Hydrogen is evolved, and aluminium chloride goes into solution; the latter then decomposes the excess of chloroform, giving off hydrochloric acid. Roughly speaking, 50 per cent of the chlorine in aluminium chloride escapes as hydrochloric acid from the chloroform solution.

MISCELLANEOUS.

Appointment.—Dr. H. A. D. Jowett, who for nearly ten years has filled the position of Senior Research Chemist on the staff of Dr. F. B. Power, Director of the Wellcome Chemical Research Laboratories, is about to leave that position, in consequence of his appointment as chief of the Experimental Department at the works of Messrs. Burroughs, Wellcome, and Co., Dartford, Kent.

MEETINGS FOR THE WEEK.

WEDNESDAY, NOV. 1st.—Society of Public Analysts, 8. "A Rapid Method for the Determination of Tin in Copper-tin Alloy," and "Water from the Simpson Tunnel," by A. G. Levy. "Dika Oil" and "Surin Fat," by J. Lewkowsitch. "Determination of Oxygen in Copper," by L. Archbutt.

THURSDAY, 2nd.—Chemical, 8.30. "Solution and Pseudo-solution—Part V., Some of the Arsenious Properties of Arsenious Sulphide and Ferric Hydrate," by E. Linder and H. Picton. "The Molecular Conductivity of Water," by P. Blackman. "Stereoisomerism of Substituted Ammonium Compounds," by H. O. Jones. "Influence of very Strong Electro-magnetic Fields on the Spark Spectra of Ruthenium, Rhodium, and Palladium," by J. E. Purvis. "The Fluorides of Selenium and Tellurium" by E. B. R. Prideaux. "Constitution of Glut-conc Acid," by J. F. Thorpe. "Some Alkyl-derivatives of Glutaconic Acid and of 2:6-Dimethylpyridine," by H. Baron and J. F. Thorpe. "Formation of β -Methylglutaconic Acid and of $\alpha\beta$ -Dimethylglutaconic Acid," by F. V. Darbishire and J. F. Thorpe.

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ON A RADIO-ACTIVE SUBSTANCE DISCOVERED IN THE TRANSVAAL AND EXPERIMENTS CONNECTED THEREWITH.*

By R. LEWIS COUSENS, M Inst.E.E.

THE discovery of a radio-active substance of which this paper forms the subject-matter, was made last year by means of certain electrical instruments which I have devised for field-work for the discovery of minerals. When examining a sample away from a certain deposit for the purpose of finding out of what it consisted, I noticed on removing the sample, which was in an ordinary sample bag, that my instruments were still affected, thus showing that there was induced radio-activity on the ground where the sample had been placed. The radio-active ore, where found, was in the form of alluvial, consisting principally of pot clay, with silica of coarser grain, and on washing this off and concentrating, I found a heavy deposit of black iron sand and other minerals, the nature of which will be more fully alluded to hereafter.

The concentrating appliances I had with me at the time were of the crudest description; a small zinc bath was used for puddling the ore; the residues were then washed over a blanket, and what we caught thereon was retained and panned in order to get rid of the remaining silica as far as possible; the residuum (the proportion of which to the crude ore was about one-fifth of 1 per cent) I regarded as concentrates.

The previous experiments were then repeated with the concentrates, a certain portion being placed in glass bottles, which were corked. I found that the ground on which the bottles were placed was made radio-active by induction, whilst if the concentrates were put into a tin there was only a very small amount of induced radio-activity on the ground underneath, thus proving that tin cuts off most of the energy that causes this induced radio-activity. From this and other experiments it appears that this induced radio-activity is not caused directly by the emanation coming in contact with the ground, as the bottles were tightly corked, but by one of the three classes of rays that are given off. By this is meant, of course, those known as α -, β -, and γ -rays, one class of which is evolved by all radio-active substances, whilst radium and thorium from one of their products emit all three.

I made rough experiments on the spot with regard to the power that different substances have of absorbing and retaining this induced radio-activity, and found that iron, lead, tin, zinc, and copper do not retain this induced radio-activity for much longer than an hour; silver, gold, and nickel for several hours; whilst platinum absorbs and retains the radiations for more than twenty-four hours after the bottle of concentrates experimented with has been removed.

On my return to Johannesburg, experiments were made to determine whether a photographic plate would be affected. A bottle of concentrates was placed on top of a key, the latter being on the photographic plate, the whole being placed within a light-tight box in a dark room. On developing the plate in the usual manner, after about twenty-four hours' exposure an image of the key was discernible; it was by no means perfect, but still it was there. These photographic experiments were continued with varying degree of success; sometimes very good radiographs were taken, at others no image appeared on the

plates, although in the majority of cases in which no image was impressed the whole plate was fogged, as if the rays of light had penetrated through all the metallic objects placed thereon.

This was proved to be frequently the case, as with two radiographs, successfully taken, of a magnet and two brass wheels, a soft iron key placed, in the one case, on the two brass wheels, and in the other across and on top of the poles of the magnet, the rays of light have penetrated through the soft iron key, the brass wheels and the edges of the magnet underneath being clearly outlined.

In all these earlier experiments the time of exposure of the plates was from twenty-four hours to three days, within a light-tight box in a dark room, and the concentrates were kept either in the containing bottle or were, immediately preceding the experiment, poured out on photographic black paper, or one or more layers of brown paper placed on top of the objects to be taken.

Experiments were also undertaken in a private laboratory, where photographic plates were affected through mica-sheet, several thicknesses of black photographic and brown papers, and aluminium plate.

Further, a tube containing a solution of iodoform and chloroform was placed in the middle of a heap of concentrates, and allowed to stand in the dark for about twelve hours, at the end of which time it was found that the colour had changed from a light yellow to a deep claret, due to the liberation of iodine.

The bottle in which the concentrates used for the last experiment were kept was left uncorked for several days, and on trying the electroscope experiment (noting the time the leaves take to collapse, by ionisation of the air between two plates, with the material under test) no result followed; the bottle was then corked for two weeks, and the experiment repeated, when the leaves collapsed in sixteen minutes. A Crookes' spintharoscope containing a small quantity of radium collapsed the leaves in four and a-half minutes, and the same result was brought about by atmospheric leakage in half-an-hour, owing to the fact that at the time wet weather prevailed.

Another sample of concentrates that had been exposed to the atmosphere at first also gave no results, but on grinding in a mortar and then placing on the test plate, the leaves collapsed in fourteen minutes.

In the meantime samples of the concentrates had been sent both to Cape Town and London for examination, and in each case the reply was received that no radio-activity could be found therein.

These replies, in face of the results that had been already obtained, were distinctly disappointing; I therefore determined if possible to carry out the work of research in a more extended manner, and accordingly applied to the Council of the Transvaal Technical Institute for permission to use their laboratory at the Institute, and my thanks are due to these gentlemen and to Professor Hele-Shaw for granting me every facility for so doing. My thanks are also due to Professors Dobson, Young, and Wilkinson for their advice, material help, and assistance when carrying out the various experiments.

The tests so far made pointed to the fact that in order to be fairly certain of obtaining results, the concentrates should be kept in a closed vessel, either during or at least preceding the various experiments, which implied that there was some very opaque substance or substances mixed with the radio-active matter, choking to a large extent the rays given out, and perhaps preventing the free generation of the emanation.

It appeared to me that the results so far obtained were caused by the rays given out by the small amount of emanation which is evolved, or its products, and which are retained if the concentrates are kept within a closed vessel, whereas if the concentrates are exposed to the atmosphere, the emanation that is evolved is dissipated in the air as fast as it is produced, and therefore results are unlikely to follow.

If this theory is correct, viz., that the results obtained

* A Paper read before the British Association (Section B), South Africa Meeting, 1905.

were caused by the emanation that is evolved, there is also the fact to be considered that the condition of the emanation itself is constantly changing, which fact was brought forward by Professor Rutherford* in the Bakerian Lecture, in which he states that the emanation changes successively into at least five different states or elements, termed radium A, B, C, D, and E, and that when in state C it gives out all three different classes of rays; when in state B it is rayless; when in states A and E it gives out α -rays only, and when in state D it gives out β - and perhaps γ -rays only. The stability of the atom, or the periods of time it takes for each product to be half transformed, is computed by him as four days from emanation to radium A; from radium to radium B, three minutes; from radium B to radium C, twenty-one minutes; from radium C to radium D, twenty-eight minutes; and from radium D to radium E, about forty years.

It may be asked, if the above theory is correct with regard to the condition of the concentrates described, why the same does not apply to the radio-active ore, viz., uranium or pitchblende found in Europe, in which there is a considerable amount of opaque minerals, but which (I believe I am correct in making this statement) will always give photographic results if a plate is exposed thereto for sufficient time?

The reply to this is that, apart from any radium that may happen to be in the ore of uranium or pitchblende, there are other radio-active substances present, and also the ore itself is radio-active, as it gives out certain classes of rays capable of affecting a photographic plate, whilst with the concentrates from the deposit described, there is only (so far as my present research goes) one kind of radio-active matter contained.

The European ore contains radium in very small quantities—according to Professor Curie about $1\frac{1}{2}$ grains per ton; the question arises would this small amount have been sufficient to have been noticed if the other radio-active substances were absent; or, in other words, would radium have ever been discovered under these conditions?

Professor Curie has stated†:—

"The radio-activity of a complex substance is generally greater the larger the proportion of the radio-active metal in the compound. Certain ores of uranium, as pitchblende, chalcocite, &c., have, however, a radio-activity superior to that of metallic uranium. We therefore questioned whether these minerals might not contain in minute proportion some substances still unrecognised and far more radio-active than uranium, and we searched by chemical methods for the hypothetical substances, always guided by the radio-activity of the substance treated."

Madame Curie, in her work on "Researches on Radio-active Substances" (Paris, 1904), gives comparative results of samples of various radio-active ores by measuring the current of electricity passing between two plates 3 c.m. apart, the air space being ionised by the radio-activity of the sample under test, multiplied by a constant of 10^{11} .

From the table of results given in this work it appears that the radio-activity of different samples ranged from the highest, 8.3 (which was a sample of pitchblende from Bohemia), down to 0.1, the radio-activity of metallic uranium being marked as 2.3.

Now, taking as an example the figures showing the greatest radio-activity, viz., 8.3, and deducting therefrom the figures representing the radio-activity of metallic uranium, we obtain a balance of 6; this figure does not represent the radio-activity of radium alone in this particular sample, but of radium, actinium, and polonium combined, the two latter elements being also found in pitchblende. The question therefore arises what proportion of the figure 6 is represented by the radio-activity of radium

alone? This is not given in the work referred to, but it can doubtless be arrived at by mathematical deduction from further experimental results; taking it, however, at 50 per cent of 6 = 3, it will be seen that with the samples showing the greatest amount of radio-activity, that of radium alone, owing to the small quantity present, is not much greater than that of metallic uranium. This statement, of course, does not apply when once the radium, actinium, and polonium have been concentrated down, the radio-activity of each of these three elements being far greater than that of uranium.

On the other hand also, if a quantity of radium is concentrated, its activity per unit is considerably greater than if this same quantity is distributed throughout a mass of ore. Professor J. J. Thomson has alluded to this point (*Smithsonian Report* for 1903, p. 201; reprinted from *Nature*, No. 1748, lxxvii., p. 601, April 30, 1903), stating:—

"Another point to be noted is that the radiation from a concentrated mass of radium may possibly be very much greater than that from the same mass when disseminated through a large volume of pitchblende; for it is possible that the radiation from one atom may tend to put the surrounding atoms in the unstable state. If this were so, more atoms would, in a given time, pass from the one state to the other if they were placed so as to receive the radiation from their neighbours than if they were disseminated through a matrix which shielded each radium atom from the radiation given out by its neighbours."

This statement also implies that the life of radium, or the stability of its atom, depends to a large extent upon whether it is concentrated or not, a point alluded to later on in this paper.

The conclusion to be arrived at is:—That the discovery of radium might not have been made at all if this element had not been combined with other radio-active substances.

It was on the assumption that the above views were correct that I commenced the experiments at the Transvaal Technical Institute.

The first point, therefore, that required investigation was to find out as far as possible the exact nature of the constituent parts of the concentrates; these were microscopically examined for me by Professor Young, who informed me that they consisted of silica, zircon, rutile (or oxide of titanium), and iron compounds in the form of magnetite and ilmenite, with perhaps a very small quantity of other metals. In order to find out if possible whether the concentrates were as opaque as I had imagined, I obtained a Crookes spintharoscope, and buried the carrier on which the small portion of radium chloride is fixed in the concentrates, at the same time covering as small a proportion of the fluorescent screen as possible. I found when I had done this that there was no fluorescence on the screen apart from that produced by the screen itself, proving that there was some very opaque matter present.

The question then arose which was the most opaque substance of those mentioned above? Professor Rutherford has partially dealt with this subject in one of his papers, in which he places lead and tin at the bottom of the list as being most opaque, iron about mid-way in the scale, whilst no mention is made of zirconium or titanium as having been examined. (See "Comparison of the Radiations from Radio-active Substances," by E. Rutherford, M.A., D.Sc., MacDonald Professor of Physics, and Miss H. T. Brooks, M.A., McGill University, Montreal; *Phil. Mag.*, vol. iv., No. 19, July, 1902).

I therefore next proceeded, for the purpose of examination, to divide up the concentrates by mechanical means as far possible into its constituent parts; the silica was carefully washed off by panning in porcelain dishes, the residuum dried, and the magnetite and ilmenite withdrawn by means of an electro-magnet. This left the zircon and rutile, which, being of nearly equal specific gravity, could not very well be separated mechanically.

It was found, as one would expect, that if the silica was washed clean there was no radio-activity in the same; there was a fair amount in the magnetite, considerably

* *Phil. Trans.*, A., civ., pp. 169–219, Bakerian Lecture, "The Succession of Changes in Radio-active Bodies," by E. Rutherford, F.R.S., MacDonald Professor of Physics, McGill University, Montreal.
† *Smithsonian Report* for 1903, p. 197. Translated from a lecture delivered by Professor E. Curie before the Royal Institution of London, as printed in the *Revue Scientifique*, Feb. 13, 1904.

more in the ilmenite, and apparently a similar amount in the zircon and rutile.

As there is probably a certain amount of titanium in the magnetite, certainly more in the ilmenite, and more still in the rutile (titanium oxide), it appears to me that in the case under review titanium is the metal which is very opaque to the rays and perhaps prevents the free generation of the emanation.

I then re-commenced a series of photographic experiments with a bottle of crude concentrates and a bottle containing the zircon and rutile for the sake of comparison.

No difference could be detected between the power of these two samples in impressing photographic negatives; an outstanding feature was that in the majority of cases the rays appeared to penetrate right through any metallic object to be photographed, and fogged the plate. For example, a radiograph of an aluminium object was taken, whilst objects of more opaque material placed on the same plate, such as gold, silver, and platinum, were not taken at all, although on repeating the experiment images of the two former were impressed on other plates. I have to add that one of the boxes in which the plates were placed during these experiments was large enough for three negatives (half size) placed horizontally edge to edge, and that frequently a dummy plate was placed therein at one end, whilst another negative was exposed to the bottle of mineral at the other. On developing the dummy plate the same came out perfectly clear, thus proving that the plates were in good condition, that there was no leakage of light from any outside source, and that the phenomena described must have been caused by rays issuing from the mineral in the bottles.

The reason of the fact that the rays frequently penetrate through metallic objects and that the plates are fogged has been explained by Madame Curie as being caused by the β -rays. These rays are deviable in a magnetic field, so that if a very strong magnet is applied in a proper manner whilst a radiograph is being taken, a sharper image of the object is the result, caused chiefly by the γ -rays impinging on the plate; the time of exposure has, however, to be lengthened. I have not yet tried an experiment on these lines, but hope to do so on a future occasion.

My next experiments were with the electroscope. Two plates were mounted on a suitable stand within a glass globe open at the lower end, the air space between the two being adjusted by raising or lowering the bottom plate to any suitable distance within the limits of about 4 inches. The upper plate was carefully insulated from earth and electrically connected to the gold leaves of the electroscope, behind which a scale was fixed in a similar manner to the arrangements devised by Professor Curie. A sample of the zircon and rutile was placed in a tube tightly corked and laid on the lower plate. The leaves of the electroscope were charged with negative electricity in the usual manner, and collapsed very slowly; in fact only slightly quicker than the effect caused by atmospheric leakage alone. The tube was then uncorked, and the contents poured into a small copper dish placed on the lower plate; the leaves collapsed 4 degrees in five minutes, but afterwards continued to do so very slowly, proving that with the dissipation of the emanation the ionisation of the air gradually decreased.

Some iron beads obtained by smelting down some of the concentrates, using lime as a flux, gave similar results. A Crookes spinthariscopes collapsed the leaves 10 degrees in eight minutes.

A cork of paraffin-wax was then fitted into the tube, through which two wires were passed in separate apertures so as to seal it, the end of one wire being coiled near the bottom of the tube and the other just underneath the cork of paraffin-wax.

This arrangement was first tried without any mineral in the tube to ascertain if the insulation was good; the leaves fell at the same rate as that for atmospheric leakage, viz., 5 degrees in twenty-five minutes.

The substance to be tested was then placed in the tube,

to a point about midway up the tube, the end of the lower wire being buried in the concentrates and the upper wire coiled just underneath the plug of paraffin-wax, the latter being electrically connected to the leaves of the electroscope, which collapsed—

5	degrees in	10 minutes
10	"	18 "
12½	"	23 "
15	"	27 "
17½	"	30 "

The above experiment was repeated with the lower wire raised above the level of the concentrates in the tube, the leaves collapsing somewhat slower, viz. :—

5	degrees in	12 minutes
7½	"	18 "
10	"	25 "
15	"	40 "

On repeating the last experiment the following day, the tube remaining corked, the leaves collapsed 5 degrees in twenty minutes, but after slightly agitating the sample, the leaves collapsed 6 degrees in ten minutes and 7 degrees in fifteen minutes. In order to increase the surface area of the material under test, the tube being rather small in diameter, a cavity was made in a block of paraffin-wax, to the bottom of which a copper coin was fixed, connected with a wire through a hole bored at the side of the block with a larger coin on top of the cavity electrically connected with the leaves of the electroscope.

As there was a large amount of atmospheric leakage, it being a wet day, careful tests were made as to the rate of fall of the leaves, putting mercury into the cavity, so as to reduce the height of the air space by about one-half. The leaves collapsed—

2½	degrees in	5 minutes
4	"	8 "

The mercury was then removed, and a quantity of concentrates poured into the cavity which occupied the same space as that of the mercury in the previous test. The leaves collapsed—

2½	degrees in	3 minutes
4	"	5 "
5	"	6 "
6½	"	8 "

A Crookes spinthariscopes of a somewhat larger size than that used in previous experiments collapsed the leaves—

10	degrees in	5 minutes
12	"	6 "

On repeating the previous experiment the following day, the leaves collapsed—

10	degrees in	6½ minutes
20	"	16 "

without previously agitating the material; after doing so the leaves collapsed—

10	degrees in	3 minutes
30	"	16 "

The test for atmospheric leakage on this day was 5 degrees in eight minutes.

On testing some ilmenite which, as alluded to before, was radio-active, and had been extracted by an electromagnet, the leaves collapsed—

10	degrees in	5 minutes
20	"	15 "

Two small samples of pitchblende and polonium used with a scintilloscope gave negative results. As, however, they were enclosed in glass cases which I did not care to disturb, the test was not a comparative one, and I would here also add that, apart from any radium that may happen to be present in pitchblende, neither the latter mineral nor polonium give off any emanation, and therefore there

would be no ionisation of the air from either of these two elements except by the rays emitted by these minerals.

My next experiments were with a mirror galvanometer.

The constant of this galvanometer was 0.0000000122 ampère per degree deflection on the scale. On testing a sample placed in the cavity in the block of paraffin-wax before referred to, and applying a steady voltage of 100 volts from the accumulator battery of 50 cells, there was practically no deflection of the galvanometer, but on testing the sample, which had been kept for some days in the test-tube fitted with the paraffin plug, as before described, the galvanometer showed 5 degrees deflection on the scale.

The current therefore passing was $5 \times$ constant of the instrument = 5×0.0000000122 ampère, and the resistance of the ionised air was 1.64×10^{10} ohms.

The above result multiplied by Madame Curie's constant of 10^{11} is 610; this is so greatly superior to any effect obtained by her with any crude sample of ore that I think the cause must be partly due to—

- a. The fact of the electrodes (copper wires) in the tube being closer together than the distance between the plates (3 c.m.) of the air condenser used by Madame Curie.
- b. The air between the top of the mineral and the plug on top of the tube was perhaps partially laden with dust derived from the mineral under test; this would increase the conductivity of the air space and give an exaggerated result.

When repeating this experiment I intend to place some cotton-wool on top of the mineral to prevent as far as possible any dust rising to the top of the tube.

The experiment of ionising the air between the secondary terminals of an induction-coil was next tried. The secondary terminals were placed apart so as to be beyond the sparking distance: on uncorking a bottle containing the minerals, sparks passed between the secondary terminals, which, however, after a time ceased, thus proving again that the emanation ionised the air, but with the dissipation of the former the ionisation decreased.

The conclusion to be arrived at from all these experiments is to confirm my previous idea, viz., the results obtained are due, principally at least, to the small amount of emanation that is given off, or its products, and therefore it is necessary to keep the concentrates within a closed vessel, at least until the experiments are proceeded with; also that fine grinding and agitating the ore causes more emanation to be evolved, thus giving improved results.

Unless these precautions are taken, results with the raw concentrates, with the usual tests, are unlikely to be obtained, at least until the opaque matter has been removed.

(To be continued).

THE VISCOSITY OF LIQUID MIXTURES AT THEIR BOILING-POINTS.*

By Dr. ALEX. FINDLAY.

ALTHOUGH a considerable amount of work has been done on the viscosity of mixtures of two liquids, comparatively few generalisations of importance have been obtained. In some cases it was found the viscosity of a mixture varied comparatively little from that calculated according to the mixture formula, while in other cases, more especially when one of the constituents of the mixture contained the hydroxyl group, marked deviations from the mixture law were obtained; the viscosity-composition curve showing a maximum or minimum point. The maximum or minimum point, further, was found to shift with the temperature at which the viscosity was determined. We are therefore met by the difficulty, here as in many other cases, of

deciding the temperature at which the determinations of the viscosity should be carried out.

So far these determinations have been carried out at one temperature throughout the whole series of mixtures, but as these investigations have been only partially successful, it was decided to determine the viscosity of a number of binary mixtures at the temperatures of the boiling-point of the respective mixtures. In this way it was thought some relationships might be discovered with other physical constants, and it was anticipated that a general relationship would be found more especially between the viscosity-composition curve and the boiling-point-composition curve. This anticipation has been only partially realised in the small number of cases so far investigated, viz., benzene-carbon tetrachloride, benzene-alcohol, acetone-chloroform, benzene-methyl alcohol. As a much larger number of mixtures must first be examined before general conclusions can be drawn, it will suffice at this stage to draw attention to the line along which the investigation is proceeding.

ALTERNATE CURRENT ELECTROLYSIS.*

By ERNEST WILSON, M.I.E.E.,
Professor of Electrical Engineering, King's College, London.

(Concluded from p. 200).

Iron.

Ferrous Sulphate (strong).—The iron plates were cut from good transformer plate and cleaned with emery paper, thereby presenting a bright but not perfectly smooth surface. Alternating currents have a marked effect upon iron in this solution. Experiment 13 was made first, and it was found that the plates lost 0.000462 gm. per sq. c.m. per hour. Without changing the solution, which during the experiment had taken up 2.4 grms. of iron, the plates, after being dried and rubbed with wash-leather to remove the surface oxide, were again inserted, and Experiment 14 made. The frequency was the same in each experiment, but the maximum coulombs were increased from 0.00956 to 0.0346. The result was to dissolve only 0.000457 gm. per sq. c.m. per hour, as compared with 0.000462 in Experiment 13, the solution again going up in density. Experiments 15 and 16 were then made with fresh solutions, but using tap-water instead of distilled. A small quantity of H_2SO_4 was added, to delay oxidation and to correct the calcium salts in the water. The result shows that 0.00389 and 0.00445 grms. per sq. c.m. per hour were thrown down, and these are roughly eight-fold the weight thrown down in Experiment 14, although the frequency and maximum coulombs are the same. The presence of some free acid in Experiments 15 and 16 may be accountable for the high figures obtained. A test sample in the solution of Experiment 13 lost 0.4 per cent of its weight in fifty-eight hours, as against 2.5 per cent of the submerged portion in seven hours in the experiment. There is considerable electrolysis. Experiment 17 was then made. In it the solution was made with distilled water acidified to the extent of 1 c.c. of H_2SO_4 in 2000 c.c. of water to delay oxidation, and nearly saturated with pure $FeSO_4$. Comparing Experiments 13 and 17 for the relation between grms. dissolved and maximum coulombs per half period, we find that 0.000229 gm. per sq. c.m. per hour should be dissolved if the relation held, as against 0.000462 observed at the higher frequency. Similar results were obtained in the cases of lead and zinc in dil. H_2SO_4 . Lead and iron give, roughly, the same ratio between the observed and calculated weights. It should be remembered that in these experiments not the whole of the plate is submerged in the solution, and there may be some additional effect at the surface of the liquid where it joins the plate.

The curve obtained in Experiment 13 between the exploring iron electrode and one plate is numbered 13 in

* Abstract of a Paper read before the British Association (Section B), South Africa Meeting, 1905.

* A Paper read before the Faraday Society. July 3, 1905.

Experiment.	Metal.	Solution.	Duration of test, in hours.	Frequency.	Density of solution.		Temperature of electrolyte C.		R. M. S., amperes per sq. c.m.	Maximum coulombs per half period.	Weight of plates, in grms.		Difference in weight of two plates after rinsing in water and drying.	Difference in weight after rubbing with wash-leather.	Average grm. per hour rinsing in water and drying.	
					Before.	After.	Before.	After.			Before.	After.				
1.	Lead.	H ₂ SO ₄ (dil.)	15	21.5	1050	1049	17.0	—	0.0236	0.0394	401.019	397.065	385.050	382.834	0.00629	(a)
2.	Do.	Do.	15	92.5	1050	1049	17.0	—	0.0236	0.0094	398.977	402.190	390.651	394.016	0.00344	(a)
3.	Do.	Do.	8	92	1050	1036	21	32	0.0847	0.0335	389.900	393.105	346.155	348.925	0.03230	(a)
4.	Zinc (amalgamated).	Do.	14½	25.5	1038	1068	17.6	19.1	0.0240	0.0345	110.58	116.67	97.98	103.08	0.00530	(b)
5.	Do.	Do.	18	92	1038	1054	21.3	22	0.0253	0.00956	101.724	104.718	96.647	99.073	0.00189	(b)
6.	Do.	Do.	7	92	1054	1066	19.5	27.5	0.0923	0.0346	95.647	99.073	88.939	91.629	0.00695	(f)
7.	Do.	Do.	8	92	1048	1055	21	25	0.0889	0.0335	115.155	109.865	112.952	107.776	0.00166	(c)
8.	Do.	Do.	32	92	1050	1058	28.5	23	0.0307	0.0334	110.120	97.935	104.760	94.500	0.00337	(c)
9.	Do.	Do.	8	92	1050	1054	28.5	25.5	0.0889	0.0335	105.147	104.457	103.810	103.133	0.00103	(c)
10.	Zinc.	Zinc chloride	12½	25.5	1255	1260	15	20.5	0.0247	0.0345	113.135	114.505	113.300	114.790	0.000116	(d)
11.	Do.	Zinc sulphate (saturated)	14½	25.5	—	—	—	—	0.0240	0.0345	109.860	115.237	Not taken	—	—	(e)
12.	Do.	Sodium sulphate	18	92	1100	1104	20	22.5	0.0241	0.00956	106.703	111.747	106.795	111.841*	0.000031	(e)
13.	Iron.	Ferrous sulphate	18	92	1114	1122	21.5	21	0.0273	0.00956	64.188	61.199	63.174	59.786	0.000462	(e)
14.	Do.	Do.	7	92	1122	1125	19.5	29	0.0979	0.0346	63.098	59.786	62.537	59.407	0.000457	(g)
15.	Do.	Do.	8	92	1174	1186	20.6	25	0.0929	0.0335	60.085	61.330	55.490	56.280	0.00389	(h)
16.	Do.	Do.	8	92	1174	1186	20.6	25.5	0.0929	0.0335	62.464	59.319	57.211	53.526	0.00445	(h)
17.	Do.	Do.	8	32	1066	1102	18.5	21.4	0.0340	0.0334	55.450	56.242	54.460	55.381	0.000787	(i)
18.	Do.	Sodium chloride	18	92	1138	1134	22	21	0.0262	0.00956	67.108*	66.242	67.190*	66.312	0.000017	(e)
19.	Do.	Do.	7	92	1134	1128	19.5	23.5	0.0929	0.0345	67.141	66.312	67.225	66.490	0.000100	(k)
20.	Do.	Do.	8	32	1086	1090	19.5	21	0.0312	0.0334	56.977	53.295	57.130	53.397	0.000121	(k)
21.	Copper.	Copper sulphate	12½	25.5	—	1105	16.25	17.3	0.0265	0.0345	138.145	140.215	138.013	140.162	0.000051	(d)
22.	Do.	Do.	8	92	1060	1092	19	30.5	0.1000	0.0335	134.550	136.875	134.527	136.717	0.000079	(d)
23.	Do.	Sodium chloride	18	92	1138	1132	21.5	21	0.0241	0.00956	134.235	133.590	134.157	133.413	0.000028	(e)
24.	Do.	Do.	8	32	1066	1098	18.4	20.3	0.0340	0.0334	134.085	133.365	133.762	133.035	0.000278	(e)
25.	Do.	Sodium phosphate	18	92	1042	1050	21.2	21.5	0.0241	0.00956	134.674	136.891*	134.682	136.892*	0.0000015	(e)
26.	Tin.	Protocloride of tin.	12½	25.5	1110	1120	16	16.8	0.0244	0.0345	123.571	119.491	123.500	119.305	0.000066	(e)
27.	Aluminium	Potash alum solution (sat.).	2	92	—	—	20.6	98	0.1030	0.0335	—	—	Not taken	—	—	(e)

Remarks.

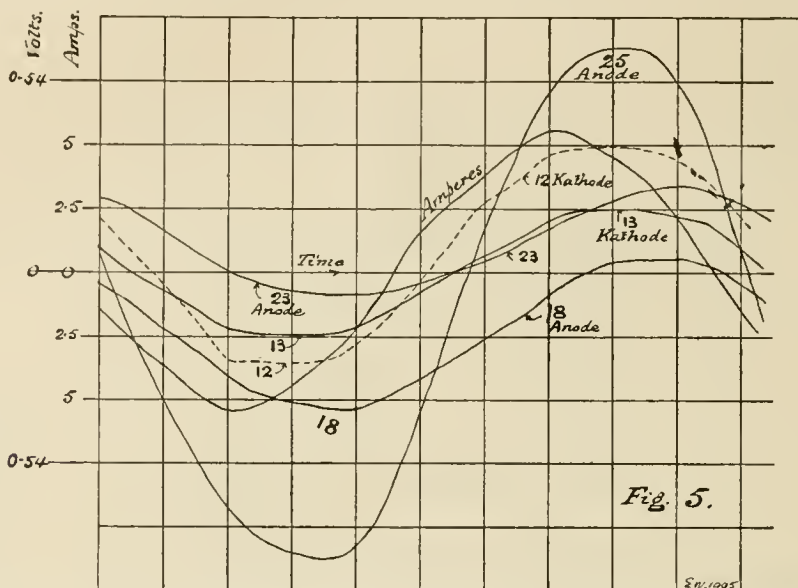
- (a) Fig. 1.
(b) Fig. 2.
(c) Fig. 3.
(d) Fig. 4.
(e) Fig. 5.
(f) Same solution as in Experiment 5.
(g) Same solution as in Experiment 13.
(h) Tap water used.
(i) Distilled water used.
(k) Same solution as in Experiment 18.

The asterisk (*) distinguishes the one plate which was rubbed with wash-leather.

Fig. 5. Its flat top indicates that the plates are fully polarised. It is considerably out of phase with the current.

Sodium Chloride (strong).—After washing and drying, the iron plates in Experiment 18 have increased in weight, but in the solution a totally submerged test sample through which no current was passed increased weight nearly to the

Sodium Phosphate Na_2HPO_4 (strong).—In Experiment 25 the copper plates were discoloured, but not diminished in weight. In Fig. 5, curve 25 gives the potential difference between a copper exploring electrode and one plate. Comparatively this potential difference is large. If correction were made for conductivity, the phase displacements might be sufficient to show almost complete re-



same percentage, so that there is no conclusive evidence of serious electrolysis. Curve 18, Fig. 5, was obtained between the iron exploring electrode and one plate. It is very much displaced with regard to the axis of time, possibly due to the fact that the plate is easily attacked when it is an anode, thereby requiring less work during that half period. When passing from the kathode to the anode states, a full quarter period in time is required before the work done on the plate becomes positive. Experiments 19 and 20 show that an increase in the weight of the plates takes place, thereby leading to disintegration.

Copper.

Copper Sulphate (strong).—In Experiment 21 the copper plates acquire a fairly easily removable copper deposit, and show slightly diminished weight. The potential difference between a copper electrode, in the solution between the plates, and one plate is given in Fig. 4, curve 21. The curve is nearly in phase with the current, and has the same wave-form. One would expect a little electrolytic action. Comparing Experiments 21 and 22, we see that although the maximum coulombs are the same, more copper is dissolved at the higher frequency, i.e., at the higher current density. The deposited copper in Experiment 22 was not so easily removable as in Experiment 21.

Sodium Chloride (strong).—In Experiment 23 the copper plates were highly discoloured, and covered with an easily removed metallic powder. The plates show diminished weight. In Fig. 5, curve 23 shows the potential difference between a copper exploring electrode and one plate. Comparing Experiments 23 and 24, we see that much more copper has been dissolved at the low frequency than the ratio of the maximum coulombs would lead us to expect. The effect is considerable in Experiment 24, and as sodium chloride is largely met with in the earth, this experiment may have practical importance. The difference would have been a little more noticeable if the detachable deposit had been removed from the surface of the plate before estimating the loss of weight.

versibility, and thus account for the small effect observed. If this were so, the effect would be similar to what has already been observed when an alternating current is passed between platinum plates immersed in dilute H_2SO_4 (see *Proc. Roy. Soc.*, vol. liv., p. 407). Dissipation of energy still occurs owing to the decomposition of the electrolyte at the plates. Any copper phosphate formed in Experiment 25 during one-half period would be reduced during the next half period.

Tin.

Protochloride (strong).—In Experiment 26 we see that 0.26 gm. of tin have gone into solution, thereby indicating considerable electrolytic action. The curve of potential difference between the exploring tin electrode and one plate is not given in Fig. 4, as there was a possibility of the electrode touching one plate during the experiment. It indicated a very small amplitude as compared with the others.

Aluminium.

Potash Alum (saturated).—A good deal of work has been done upon aluminium in connection with alternate currents. It is known that the film formed on the surface offers considerable resistance to the electric current (see *Proc. Roy. Soc.*, vol. lxiii., p. 329). In Experiment 27 two aluminium plates were immersed in a saturated potash alum solution, and owing to the formation of a surface layer the internal resistance gave rise to such dissipation of energy that the solution was boiling after the experiment had progressed three-quarters of an hour. The plates were very much eaten away in places, but quite bright where they had been protected by the surface layer.

In conclusion, I wish to express my thanks to Professor E. F. Herroun for valuable suggestions. Mr. D. Sheppard worked with me all through and prepared the experiments. Mr. T. Mitchell has also rendered assistance, and has worked out some of the results. To these gentlemen I tender my thanks.

OBSERVATIONS ON COLUMBIUM AND TANTALUM.

By EDGAR F. SMITH, University of Pennsylvania.

IN 1801, Hatchett, while studying minerals in the British Museum, came upon a specimen from Haddam, Conn., which attracted his attention because of its rather high specific gravity and its brilliant black colour. A portion of this material was given him for examination, with the result that he discovered in it a new metallic acid, to the metal of which he applied the name columbium. It was his earnest hope that he might obtain larger quantities of the American mineral in order to exhaustively study the new element, and it is of interest to remark that Hatchett fondly expected this material assistance from Thomas Peters Smith, a member of this Society and an enthusiast in chemical science, who on his return from England met an untimely death on shipboard.

In 1802, Ekeberg, of Sweden, while examining an unknown mineral, found that it contained a new metallic acid, to the metal of which acid he assigned the name tantalum, because "when placed in the midst of acids it is incapable of taking any of them up and saturating itself with them." Later, Wollaston (1809) strove to prove that columbium and tantalum were identical. In this he failed. The few reactions known even at that early day differentiated the new elements. About 1840, Heinrich Rose, in studying similar minerals from other localities, came to the conclusion that the American mineral contained an element absolutely different from tantalum, and called it niobium. Subsequently, owing to his inability to account for the peculiar products which he got by chlorinating a mixture of the oxide of the new element and carbon, he asserted that, in addition to niobium, there was present pelopium (1846). Later (1853), however, he seems to have arrived at the opinion that niobic acid and pelopic acid were different oxides of niobium. The first he called niobic acid and the second hyponiobic acid. Hermann also contributed to the uncertainty which surrounded the two elements (columbium of Hatchett and tantalum of Ekeberg) in that he announced the existence of ilmenium; but it was not generally accepted by chemists. Hermann, however, persisted in his declaration that it occurred along with the other two elements to which reference has been made. Von Kobell believed that he had detected dianium in allied minerals. This unfortunate state of affairs prevailed until the early sixties, when Marignac, after a careful study of a number of minerals from various localities, announced the existence in them of but two elements—the columbium of Hatchett and the tantalum of Ekeberg—and added that the confusing reactions which had perhaps led Heinrich Rose—but most certainly, Hermann and von Kobell—astray were to be explained by the presence of titanium in all tantalites and columbites. It is only fair to say that Marignac never succeeded in obtaining titanium from any one of the minerals in which, according to him, it occurred, associated together with columbium and tantalum. Indeed, in his concluding paper on columbium he frankly acknowledged that the columbium compounds which he used for the determination of the atomic weight of the metal, contained titanium, and that he knew of no method by which the latter could be separated from columbium. Marignac's conclusion was accepted by the chemists of the world as final.

When we come to examine the evidence which Marignac gives for the presence of titanium, we find that it is, practically, that the re-crystallisation of a double fluoride of columbium and potassium, supposed to contain titanium, gave rise, gradually, to a fraction which became more insoluble in water, and the molecular weight of its acid oxide approached, within ten or more units, that required by titanic oxide. It is well to bear in mind that at no time did Marignac, whose ability and keen insight one would not for a moment question, give any tests which are

ordinarily regarded as indicating titanium. He assumed it to be present on the evidence mentioned above, viz., the greater insolubility of the double fluoride and an approximate molecular weight corresponding to that required by titanic oxide. Ever since Marignac's day chemists the world over have tacitly accepted titanium as associated with columbium in columbites. They have also estimated its quantity by methods suggested from time to time. One of these methods is based on the colour reaction which titanium salts give with hydrogen peroxide. Its intensity, compared with that shown by a known amount of titanium, has been regarded by most analysts as entirely satisfactory. For the determination of the amount of titanium in columbium many methods have been proposed, but this is not the place to discuss them or their value.

As late as 1877, in the last paper published by Hermann, he announced the element neptunium, and claimed to have obtained it from the acid mother-liquors remaining after tantalum potassium fluoride, ilmenium potassium fluoride, and columbium potassium fluoride had been crystallised out. The particular mineral in which he observed it was a columbite from Haddam, Conn.: in other words, the same mineral in which columbium had been originally discovered by Hatchett.

The existence of neptunium has never been contradicted. This is probably because the majority of chemists thought that the verdict in regard to the constitution of tantalites and columbites had been given by Marignac, and that the numerous, unusual reactions of the metallic acids contained in those minerals, noted and commented upon at various times by Heinrich Rose, von Kobell, Blomstrand, and Hermann, were all due to the contaminating influence of titanium.

The two elements, columbium and tantalum, in their derivatives, have received comparatively little attention within the last quarter of a century, although at intervals attempts have been made to clear up the mystery which, in a certain sense, surrounds them. In this laboratory, several investigations upon derivatives of them have been made. These being not wholly satisfactory, about three years ago, 50 lbs. of columbite from South Dakota and 25 lbs. from Haddam, Conn., were worked up, with a view of getting an abundant supply of starting-out material; with the view, also, of studying anew the various derivatives of both columbium and tantalum. In the year 1903-1904, Dr. R. D. Hall devoted, in this laboratory, much time and labour to the double fluorides of tantalum and columbium. He made a comparative study of the reactions of the same with the reactions of titanium. His results have been published, but from an examination of them it will be observed that he was not able to find any tests, while using the double fluorides, which differentiated titanium from columbium so thoroughly that he could expect to obtain a complete separation of these two most interesting elements. It is true that he was able by precipitating potassium columbium fluoride incompletely with ammonia, to get a columbium oxide, which apparently gave no response to the hydrogen peroxide test upon its application, or to the reagent called chromotropic acid. Hence he inferred that he had eliminated the titanium from the columbium. More recent work with large quantities of material has demonstrated that in the latter cases it was impossible to entirely remove the metallic acid which gave the colour tests. It was further found that by the action of sulphur monochloride upon the oxides of columbium and titanium, corresponding chlorides were produced; but again, it proved impossible to wholly expel the titanium from the columbium by this process, notwithstanding titanium chloride is an exceedingly volatile liquid and columbium chloride a solid crystalline body.

In the present year, we have, in this laboratory, prepared large quantities of the double fluoride of tantalum and potassium, and found no difficulty whatsoever in eliminating from it every trace of what was supposed to be the titanium double fluoride.

Having thus, at our disposal, such generous amounts of pure tantalum oxide, free from columbic oxide—in short, really pure tantalum oxide—it was determined to make a new study of the double fluorides of tantalum with the alkali metals and organic bases. This was undertaken in order to discover, if possible, why Dr. Pennington, when working in this laboratory in 1895, obtained double fluorides of tantalum and columbium with caesium, which showed these unusual formulæ, $15\text{CsF} \cdot \text{TaF}_5$ and $7\text{CsF} \cdot \text{CbF}_5$, which varied so widely from those generally followed by the double fluorides of tantalum and columbium, and were not in accord with the law proposed for double halides (*Am. Chem. Journ.*, v., 291).

At the outset it was thought that this re-investigation of the double fluorides would prove to be an easy and simple matter. But it was not long until it was seen that the discordant results of Dr. Pennington were probably due to the fact that there was more than one caesium tantalum fluoride. Indeed, the latest work done in this laboratory, by Mr. C. W. Balke, proves that there are two caesium tantalum fluorides, two rubidium tantalum fluorides, two sodium tantalum fluorides, two ammonium tantalum fluorides, and so forth, of these ratios:—

$\text{TaF}_5 \cdot \text{CsF}$	$2\text{TaF}_5 \cdot 3\text{RbF}$
$\text{TaF}_5 \cdot 2\text{CsF}$	$\text{TaF}_5 \cdot 2\text{NaF}$
$\text{TaF}_5 \cdot 2\text{NH}_4\text{F}$	$\text{TaF}_5 \cdot 3\text{NaF}$
$\text{TaF}_5 \cdot 3\text{NH}_4\text{F}$	$\text{TaF}_5 \cdot 2\text{KF}$

The existence of several such double fluorides with each of the alkali metals naturally raises the question whether these salts ought to be used for the determination of the atomic weight of tantalum, inasmuch as each salt is likely to be contaminated with smaller or larger quantities of the other, depending upon the condition or the care with which they are prepared. Marignac used potassium tantalum fluoride and ammonium tantalum fluoride in his re-determination of the atomic weight of tantalum. It would seem, from the study of the salts just mentioned, that even this skilled and careful analyst could not have been sure that he had a definite homogeneous body in the determinations which he made. Of course, if there was even a slight amount of a second salt in the salt used for the atomic weight work, it would naturally vitiate the final result. Of all the double fluorides of the alkali metals and bases with tantalum which have thus far been studied by Mr. Balke, that of sodium and tantalum, of the ratio 3 to 2, seems to be the one having some definite and most stable characteristics. We hope to re-determine the atomic weight of tantalum, but it is not probable that we shall use any one of the double fluorides of which mention has been made, although they appeal strongly because of the ease with which they can be crystallised. The uncertainty, however, as to whether they are really absolutely of one definite ratio every time that they are crystallised is uncertain. Hence they had better be abandoned in atomic weight determinations.

The question may also be asked, may not the double fluorides of columbium with the alkali metals which have been used for atomic weight purposes been contaminated with salts of varying ratios? This point will receive attention.

Turning again to columbium, it seems proper to record that, having eliminated the tantalum completely from a mixture of oxides obtained from Haddam columbite, the remaining potassium columbium oxyfluoride was crystallised a number of times from water, and also from solutions containing much hydrofluoric acid. This procedure finally gave a mother-liquor that was decidedly acid. A metallic acid remained in this mother-liquor. According to Hermann, in his communication of 1877, this acid should be neptunic acid. Therefore, the acid mother-liquor was treated as directed by Hermann, namely, it was evaporated, the residue was dissolved in water, and the boiling solution precipitated with an excess of caustic soda. The precipitate, after the liquid had become cold, was filtered out, pressed thoroughly from adherent water, and then

boiled with twenty-five times its own weight of pure water. Everything dissolved. The solution was perfectly clear. On cooling, there separated from it the beautiful needle-like crystals of sodium columbate. According to Hermann, the precipitate which was collected, pressed out and then boiled with water, should, if neptunium were present, have left a slimy mass, insoluble in water. This, Hermann said, was sodium neptunate. It should be observed that our experiments were made with the final acid liquors obtained from the double fluorides present in columbite from Haddam; further, that we proceeded in strict accordance with the directions of Hermann, and having done all this, did not obtain a gelatinous mass which might have been sodium neptunate. In Hermann's communication, to which reference has been made so frequently, he lays great stress on the fact that the distinguishing reaction of neptunium is the beautiful golden-yellow colour which sodium neptunate imparts to a salt of phosphorus bead in the *reducing flame*. It is needless to add that we tried on different occasions to find neptunium, according to the directions of Hermann; but our search was fruitless. On one occasion, however, we obtained a mass, not great in amount, which, in the inner blowpipe flame, did impart a yellow colour to the salt of phosphorus bead, but more careful examination of this residue demonstrated that it contained tantalum, iron, and some columbium. The intense golden-yellow colour, which was so strongly emphasised by Hermann, we could not get; so that it is very probable that neptunium, like ilmenium and the other metals announced from time to time as present with columbium and tantalum, must really be placed in the list of defunct elements. It has not been our wish to bury this candidate for elemental honours. Indeed, we would have been only too glad to have found the evidences of its existence, and to have confirmed the observation of that earnest and sincere student of chemical science, who, in his tireless labours, frequently felt confident that he had fallen upon the cause of the varying results observed with columbium and tantalum.

In this connection it may be added that, having freed the tantalum and columbium oxides as thoroughly as possible from ordinary contaminations, the problem of removing tungsten and tin confronted us. After much experimentation, we found that the certainty of the removal of these impurities could only be had by fusing the tantalum and columbium oxides with sodium carbonate and sulphur. It is true that small quantities of tantalum and columbium will be lost, being carried along with the tungsten and tin, but as we were seeking a method of purification and not a separation, we adopted this course. It is the one which was pursued by Heinrich Rose. Our own experience leads us to say that the removal of tungsten and tin from columbium and tantalum oxides cannot be realised by digestion with ammonium sulphide. Indeed, not only did we find the fusion with the sodium carbonate and sulphur necessary, but that working in large quantities of material, as in our case, two and three refusions with these reagents were found necessary. Another point of interest in connection with the purification of the tantalum and columbium oxides may be mentioned. It has frequently been said that in crystallising out the double fluorides of these metals, if titanium be present with them, it will be found in the potassium tantalum fluoride. We have encountered no difficulty in getting potassium tantalum fluoride perfectly free from what is supposed to be titanium by one or two crystallisations. It has been assumed that, as potassium titanium fluoride is rather insoluble in water, it would naturally go with potassium tantalum fluoride. This, however, seems to be an incorrect observation. It masses with the columbium potassium fluoride; at least the element which gives the yellow colour with hydrogen peroxide, or a rose-red with chromotropic acid, is always found associated with the columbium. How to free the columbium from titanic acid we do not know. We are in precisely the same position as that of Marignac, notwithstanding we have probably made greater efforts than he to

remove it from the columbium. It is this point in our investigation upon which we have been continuously at work for the last year. We have tried fractional precipitation with ammonia water, fractional crystallisation of the double fluorides, fractional chlorination of the oxides in the presence of carbon and the action of numerous organic bases, without finding any way of effecting a separation. Indeed, the separation of columbium and titanium is a problem which the analyst has not solved up to the present. As remarked, it has received and is receiving our daily attention. Once having achieved this result, and having definitely determined the character of the colour-giving metallic acid, or proved it to be titanium, without any further doubt, we then hope to subject the purified columbic oxide to a searching review in all its derivatives, just as we are now doing with the compounds of tantalum. In anticipation, it may be said that there are some most interesting complexes of tungstic acid with tantalic oxide, and also of tungstic acid and columbic acid. These are under study at present. These complexes, also, have brought analytical problems that are most puzzling. Yet our progress with them leads us to hope for a separation and a satisfactory solution of the same.

Some attention has likewise been given to per-tantalates and per-columbates. It would not be the least surprising to find these derivatives answering admirably for atomic weight work.—*Proceedings of the American Philosophical Society*, 1905, xlv., p. 151.

NOTICES OF BOOKS

Physical Chemistry and its Applications in Medical and Biological Science. By ALEX. FINDLAY, M.A., Ph.D., D.Sc. London, New York, and Bombay: Longmans, Green, and Co. 1905.

THESE lectures, which were delivered before the University of Birmingham, were intended specially for the benefit of students of medicine and biology, to give them an elementary introduction to the application of physical chemistry to these sciences. The lectures deal with elementary conceptions regarding osmotic pressure, the theory of ionisation, and the study of the disinfective and toxic action of ions, the permeability of membranes and adsorption catalysis, and colloidal solutions. Thus it will be seen that they touch upon a considerable range of subjects, and cannot be expected to do more than point out the leading features to be noticed; considering all things, the small amount of chemical knowledge the audience might be supposed to possess, and the limited time at the lecturer's disposal, he has been wonderfully successful in imparting a considerable amount of valuable information in a lucid and interesting manner, and the book will be of great use to the biologist who wishes to become familiar with the applications of physical chemistry to his branch of science, and to whom the author looks for advances as regards the solution of biological problems.

Soils and Fertilisers. By HARRY SNYDER, B.S. Second Edition. Easton, Pa.: The Chemical Publishing Co. 1905.

THE changes made during the revision of the text of this work, and the extensive and important additions, have altered its scheme to such an extent that a change of title seemed advisable. As it now stands it gives a full account of the chemistry of soils, the use of all kinds of fertilisers, and the food requirements and rotation of crops, together with outlines of the laboratory practice necessary to illustrate the text, and it appears all that could be desired for the use of those who, without aspiring to the acquirement of a large

amount of scientific knowledge, wish to become acquainted with the chemical principles underlying the art of the farmer, and to be capable of dealing in an intelligent spirit with the problems with which he is confronted, without falling back on mere rule-of-thumb methods.

Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie. ("Modern Conceptions in the Sphere of Inorganic Chemistry"). Braunschweig: Friedrich Vieweg und Sohn. 1905.

THERE is probably no chemist living who is better qualified to write upon modern developments in the theory of inorganic chemistry than Prof. Werner, and his book deserves the careful attention of all interested in the study of this subject. The book, which is one of a series of monographs on scientific and mathematical topics, gives a complete account of the views of the author and of other eminent chemists regarding the structure and spacial arrangement of the molecules of inorganic substances, and while the author aims at giving broad outlines rather than details, the treatment is, comparatively speaking, very full. The subject is divided into three sections. In the first of these is explained the modern development of the idea of an element and of the Periodic System, with special reference to Prof. Werner's own theory relating to this system. The second part deals shortly with compounds of the first order, and with the doctrine of valency, while the last section, which forms the greater part of the book, gives a complete *résumé* of compounds of higher order, and of the doctrine of co-ordination, in which region the author has done so much exceedingly valuable work.

CORRESPONDENCE.

INSTITUTE OF CHEMISTRY EXAMINATIONS.

To the Editor of the Chemical News.

SIR,—I note with pleasure the letter from your correspondent "One of Many" on the above subject (*CHEMICAL NEWS*, xcii., p. 200). His remarks about obtaining the F.I.C. by way of the B.Sc. are true and very appropriate.

As regards the excellent scheme he has outlined I have only one exception to make, namely, that in my opinion Stages III. and IV. (Mathematics) are going rather beyond the requirements of most technological chemists. Stage II. appears to me to be amply sufficient. In this connection I may say that even in the B.Sc. (London) Examination the syllabus is now so arranged that Mathematics in its higher stages is not so compulsory as formerly, and the subjects for the Inter. B.Sc. do not necessarily include Mathematics.

I would venture to suggest that in place of the higher Mathematics, Natural Sciences be substituted, since they are of importance and use to chemists. I refer more particularly to Heat and Light, Magnetism and Electricity, which are entirely omitted from your correspondent's scheme. It is only by the adoption of some such arrangement as proposed by "One of Many" that many technological chemists can obtain anything like a recognised "hall-mark" in their profession, and at the same time convert the, at present, almost valueless certificates into something of more generally recognised merit.

In conclusion, I trust that "One of Many" will take my criticism of his scheme in the right spirit. I can assure him that I am obliged for his taking up the subject in so able a manner.

Apologising for the trespass on your space, I am, &c.,
TECHNICUS.

CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 15, October 9, 1905.

Derivatives of Cyclohexane.—P. Freundler and E. Diamond. — The authors prepare bromocyclohexane ($C_6H_{11}Br$) and iodocyclohexane ($C_6H_{11}I$). These derivatives do not condense easily with the sodium derivatives, on account of their tendency to decompose into cyclohexane and the hydricid. Only traces of the normal product of the reaction can be obtained by heating the chloride or iodide with sodium acetylacetic ether, either in presence of absolute alcohol at 100° in a sealed tube or in xylene solution at 150° . The former method gives slightly better results. In addition to these products, the following were also prepared: — Cyclohexylcyanacetic ether, $C_6H_{11} \cdot CH < \overset{CN}{CO_2C_2H_5}$; cyclohexylmalonic ether, $C_6H_{11} \cdot CH(CO_2C_2H_5)_2$; and cyclohexylacetic or hexahydrophenylacetic acid, $C_6H_{11} \cdot CH_2 \cdot CO_2H$. The ethylic ether prepared from absolute alcohol and hydrochloric acid gas is a liquid of pleasant smell which distills at $211-212^\circ$ at 766 m.m. pressure.

Decomposition of Meta- and Para-nitrobenzylic Alcohols under the Influence of Aqueous Soda and Alcoholic Soda.—P. Carré. — Meta- and para-nitrobenzylic ethers, in the same manner as the ortho-nitrobenzylic alcohol, when in alkaline solution show phenomena of oxidation and reduction depending on their nitro-grouping and their alcohol-grouping. The stability of these three nitrated alcohols towards alkalis increases from the ortho- to the meta-derivative. The decomposition of the ortho-alcohol is distinguished from that of the meta- and para-alcohols by its greater rapidity, and by the formation of substances which result from the facility of reaction of the groups situated in the ortho-position, whilst the meta- and para-alcohols give exclusively products which result from the oxidation of the alcohol group and from the reduction of the nitrated group. Ortho-nitrobenzylic alcohol can be further distinguished by the presence of amine substances in the products of decomposition, these latter not being formed in the case of the meta- and para-nitrated alcohols.

Certain Phenolic Ethers having a Pseudo-allylic Chain, $ArC(CH_3)=CH_2$.—MM. Béhal and Tiffeneau. — In a former research the authors discovered the conditions of preparation and the physical constants of certain aromatic pseudo-allyl derivatives. They now investigate the properties and reactions of these derivatives when subjected to hydrogenation, oxidation, and fixation of IOH.

No. 16, October 16, 1905.

Absolute Desiccation of Vegetable Substances.—L. Maquenne. — The author makes a series of experiments on the desiccation of vegetable matters, and finds that amyl bodies, and especially pure starch, can be easily and rapidly desiccated in dry air. Under these conditions the loss of water is greater than in a stove. The grains of starch also dry better in a vacuum at 40° than in air at 170° . The author formulates his conclusions as follows:—1. The constancy of weight of a vegetable product (probably also the majority of mineral and organic substances), after remaining some time in a stove in ordinary air, can at no temperature be considered as perfectly desiccated. 2. The use of an ordinary stove is absolutely useless for the rigorous analysis of very hygrometric bodies such as starch. 3. The absolute desiccation of such substances can only be effected even at a high temperature in a medium absolutely free from water-vapour. It is apparently complete in one hour by

heating at 120° and two hours at 100° in a current of dry air. Under these circumstances the matter remains unchanged, and the proportion of water is found to be less by 1 per cent than that which is present after a much longer period of desiccation by the ordinary methods.

Basicity of Pyranic Oxygen. Halogen Combinations of Dinaphthopyryl with Metals and Metalloids.—R. Fosse and L. Lesage. — The radical dinaphthopyryl, $—CH < \overset{C_{10}H_6}{C_{10}H_6} > O$, forms a large number of double salts with the halogens and mineral elements in the same manner as potassium. In the present paper the authors give the formulæ of new halogen double salts containing dinaphthopyryl and one of the elements, platinum, lead, iron, zinc, tin, bismuth, arsenic, and antimony,

MISCELLANEOUS.

Issue of Work of Art on Gunpowder.—Mr. Oscar Guttman, M.Inst.C.E., F.I.C., F.C.S., of 12, Mark Lane, London, E.C., intends to publish a facsimile reproduction of all ancient pictures and engravings dispersed in libraries all over the world, referring to the invention, early manufacture and examination, and first use of gunpowder. It is to be a work of art, printed by hand on the finest handmade paper, with an imitation fifteenth century binding, and limited to about 300 numbered copies. The publication is made in the interests of science, not only without profit, but by selling a number of copies for collectors at a higher price, the subscribers will get it under cost price. Scientific and industrial men who have not received a direct invitation should apply for particulars to Mr. Guttman.

The Milan International Exhibition, 1906.—Celebrating the opening of the Simplon Tunnel, the first International Exhibition held by the Kingdom of Italy will be opened at Milan on April 15th next. It will be under the high patronage of the reigning monarch and supported by a powerful British Commission, of which Mr. Arthur Serena has been appointed Honorary Executive Commissioner. The Commission also includes Lord Brassey, Sir Albert Rollit, M.P., Sir William Holland, M.P., Comm. L. Allatini, Cav. P. Polenghi, and others, with as Joint Secretaries Mr. Kenric B. Murray (London Chamber of Commerce), Sir Edward Fithian (Associated Chambers of Commerce), and Sig. Tullio Sambucetti (Italian Chamber of Commerce). The British Government have voted the sum of £10,000 to the National Section. H.M. the King of Italy will offer prizes to the extent of £1600 to exhibitors. This amount will be divided as follows:—

1. A prize of £200 for automatic safety couplings for railway rolling stock.
2. A prize of £200 for the best method of testing high voltage electric currents without danger to the operator.
3. A prize of £400 for the best and most original exhibit of machinery or manufacturing process.
4. A prize of £200 for the best established method of distributing healthy and pure milk in centres of population.
5. A prize of £400 for the best type of popular dwelling adapted to the climate of northern Italy.
6. A prize of £200 for motor boats.

In addition to the foregoing there will be given a National Prize of £200 to the public institution or private society which, during the last ten years, has been most successful in the work of reclaiming waste lands in mountainous districts, and in the improvements of pasturage. The Exhibition will occupy close on 200 acres, of which the buildings will occupy 42. Among the other leading nations that will be officially represented are included France, Germany, Austria, the United States, &c. Of the ten sections the Exhibition will be divided into, only one, that

of Fine Art, is national. The others include Land, Sea, and River Transportation (Locomotives, Motors, Trams, Carriages, Ship Models, Shipping Equipment, Nautical Instruments, &c.), Aeronautics, Meteorology, Manufacturing and Decorative Arts, Machinery in Motion, Social Economy, Agriculture, Hygiene, Fisheries, &c. These special inducements to exhibiting will doubtless possess attraction for British manufacturers, inventors, and others, who should without loss of time address themselves for further particulars to the Hon. Executive Commissioner of the British Section, 1 and 2, Oxford Court, Cannon Street, London, E.C.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—Royal Institution, 5. General Monthly Meeting.
Society of Chemical Industry, 8. "Evaporation in
vacuo of Solutions containing Solids," by J.
Lewkowitsch.

FRIDAY, 10th.—Physical, 8. "The Question of Temperature and
Efficiency of Thermal Radiation," by J. Swinburne.
"Note on Constant-deviation Prisms," by T. H.
Blakesley.

ERRATA.—P. 173, col. 2, line 12 from top, for 21963'697 read 21963'258.
Line 30 from top, for 14'575 read 14'0575.

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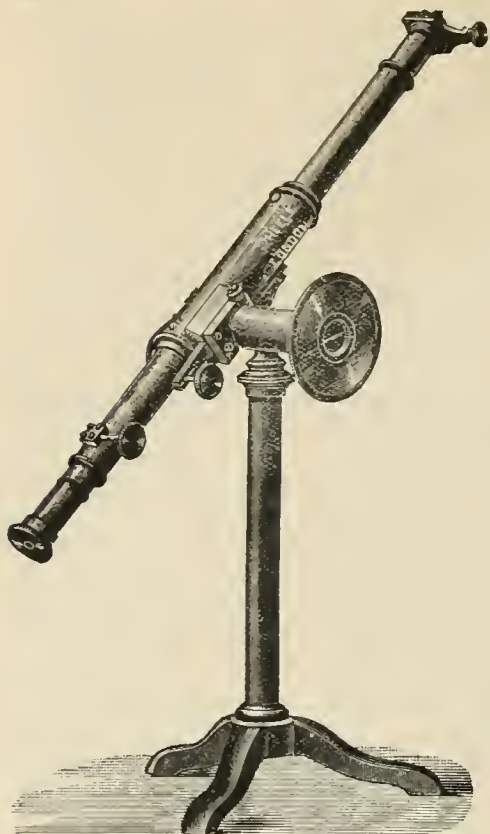
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REPRINTED from the CHEMICAL NEWS.

CONTENTS.

Introduction.—Historical.—Chap. I. Radio-activity of
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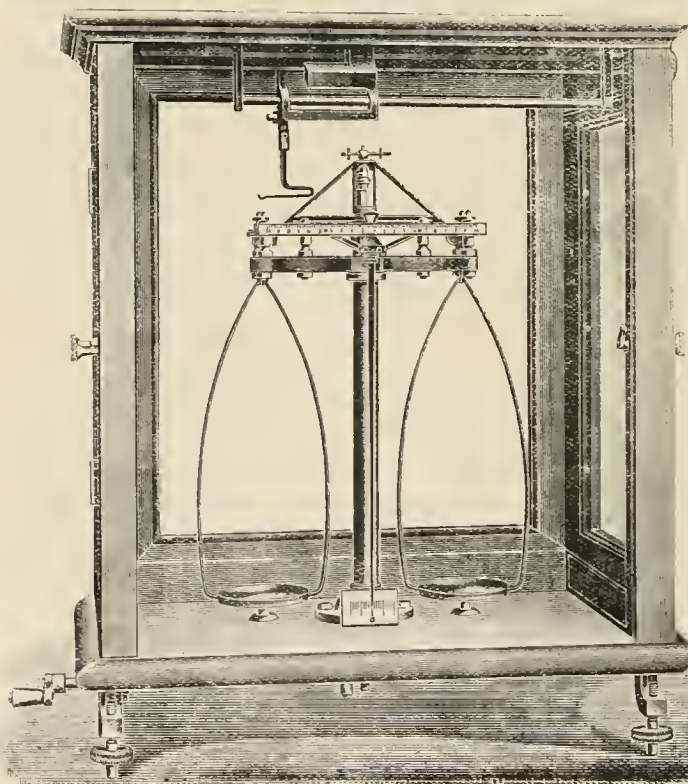
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THE CHEMICAL NEWS.

VOL. XCII., No. 2398.

ON A RADIO-ACTIVE SUBSTANCE DISCOVERED IN THE TRANSVAAL AND EXPERIMENTS CONNECTED THEREWITH.*

By R. LEWIS GOUSENS, M Inst.E.E.

(Concluded from p. 2068.)

CHEMICAL experiments were then undertaken with a view, if possible of getting rid of the opaque matter, which, as stated before, appeared to be titanium. A small quantity of the zircon and rutile was smelted down, using carbonate of soda as a flux.

The residue was then treated with hydrochloric acid and put into solution. After standing for several hours a small amount of precipitate of a whitish colour was formed, which was increased by adding ammonium hydrate; this was filtered off, and the precipitate obtained I will refer to as No. 1.

Ammonium chloride was then added, and No. 2 precipitate of a reddish colour was brought down. The solution was again filtered off, and ammonium carbonate added, resulting in No. 3 precipitate of a light grey colour. Sodium phosphate was then added to the filtrate, in which, after standing for several days, no further precipitate was observable. The solution was then evaporated down, leaving behind the sodium and potassium carbonates, which I will allude to as precipitate No. 4.

Precipitate No. 2, of a reddish colour, showed the presence of ferric iron. Although the greater portion of this metal had been extracted by magnetic means (as before described) there are certain compounds of iron which are non-magnetic, which accounts for its existence in this precipitate. I found that—

No. 1 Precipitate was slightly radio-active.

No. 2 Precipitate was the most radio-active of the four precipitates.

No. 3 Precipitate was non-radio-active.

No. 4 Precipitate was strongly radio-active at first, the radio-activity then decaying to a point I would call fairly radio-active, it then remaining constant.

As precipitate No. 4 was apparently free from opaque matter, I tried its effect on a photographic plate; the experiment so far succeeded that a portion of the image of the object, which was a small brass wheel, was impressed thereon. The original quantity, however, of the concentrates treated was very small, viz., about 3 ounces, and, moreover, the object of the chemical experiment was not only to get rid of the opaque substance, but if possible also to bring down all the radio-active matter into one precipitate; in this I had not so far succeeded, because, as detailed above, the radio-active matter was distributed over three of the precipitates in varying quantity, the apparent reason for this being alluded to hereafter.

A larger quantity of the concentrates therefore was then treated, the method of procedure being slightly varied. After smelting down with carbonate of soda as a flux, and steeping the product in strong hydrochloric acid, which was boiled, distilled water was added; a fair amount of precipitate made its appearance containing silica with a small proportion of iron, which I shall allude to as precipitate A. This was extracted by filtration, and on adding ammonium hydrate and ammonium chloride to the filtrate, a further precipitate (B) was obtained. Precipitate C was obtained

by adding ammonium carbonate to this filtrate; the solution was filtered again, and on adding sodium phosphate no further precipitate was observable. The solution was then evaporated down, leaving behind carbonate of soda, &c., which I shall allude to as precipitate D.

Precipitate A was very slightly radio-active, less than No. 1 precipitate in the first experiment.

Precipitate B was more radio-active than any sample of concentrates or precipitates in my possession up to that time.

Precipitate C was non-radio-active.

Precipitate D was strongly radio-active at first, decaying in a similar manner to that of No. 4 to a point when it became constant.

This experiment was more successful than the previous one, as I had now obtained a greater proportion of the radio-active matter in the one, viz., precipitate B. Both precipitate 1 and precipitate D were at first very active, but the radio-activity (as stated above) decayed after a time to a point considerably below that of precipitate 2 and precipitate B, afterwards remaining constant.

That any radio-active matter should finally come down with the carbonate of soda was at first somewhat surprising, as precipitate 3 and precipitate C were absolutely non-radio-active.

I have come to the conclusion that this is due to the product of the emanation and not to any of the original radio-active matter, all the latter having, in my opinion, come down in the first two precipitates, principally in the latter of these two.

My reasons for coming to these conclusions are:—

1. That from experiments already made, the radio-active matter being combined with the titanium and iron (I believe the zircon when separated out will be found to be non-radio-active), has come down with these metals in precipitates A and B.

2. Precipitate C is non-radio-active.

3. That according to Professor Rutherford (I shall frequently quote this investigator as my authority in the argument), all the products of the radium emanation are soluble in strong acids and partly so in ammonia. In the publications of this *savant*, and those of other authorities, I can only find one method that has been adopted of precipitating these products, i.e., by evaporating down the solution in which they have been dissolved. It is only reasonable to suppose, therefore, that when hydrochloric acid was added to the concentrates which had been smelted down with carbonate of soda, that the products of the emanation remained in solution until the latter was finally evaporated down, leaving behind the said products with the carbonate of soda.

4. The character of the radio-activity of this residual product, viz., it was very active at first and then decayed down to a constant quantity. This is the character of the product of radium when it arrives at the state known as radium D, which rises again in activity several months afterwards, remaining in this state for about forty years.

I have lately tested this precipitate, which is about four months old, and find that its activity is rising again, so that it appears to correspond with the product known as radium D.

The corollary of the above statements also is that I believe the radio-active substance to be radium, not only for the reasons already given but also for the following:—

The final products of both thorium and actinium (the only two known elements in addition to radium from which an emanation is evolved) have been found, and are known as thorium C and actinium C. Both of these final products are rayless, i.e., give forth no radio-activity. Now sufficient time has by now elapsed for the product of the emanation from the radio-active matter in the concentrates to have reached the final product, assuming the same to be either actinium or thorium, and therefore in either case it should be non-radio-active. As, however, it is radio-active it cannot be derived from either thorium or actinium.

* A Paper read before the British Association (Section B), South Africa Meeting, 1905.

On the other hand, the final product of radium has not yet been found, and according to the time given by Professor Rutherford representing the periods necessary for the successive changes to take place, the product of the emanation from the radio-active matter in the concentrates should be in the state radium D if it is this element. Tests tend to prove that this is the case, as radium D is radio-active, giving out β -rays, and the radio-activity remains fairly constant over a considerable space of time.

Precipitates 4 and D are radio-active, and otherwise appear to coincide with the characteristics of the element radium D.

I may mention that the total period of time as given by Professor Rutherford necessary for 50 per cent of thorium products to be successively transformed from the emanation down to the final product thorium C is eleven hours, fifty-six minutes. Now supposing this period had not elapsed between the time when the carbonate of soda was brought down with the products of the radio-active matter and the time when the latter was tested for radio-activity, it is impossible to understand how it could have been derived from thorium, because with thorium the rate of decay of the activity of its products decreases in each period, according to a simple exponential law, with the time. Now the activity of radium products does not decay throughout the whole range of their successive changes in accordance with the above law, neither does the activity of precipitate 4 or precipitate D do so, and are therefore *dissimilar* to the results obtained with thorium products, and *similar* to those obtained with radium products.

Having obtained a precipitate, viz., B, that was more radio-active than any other sample in my possession, and which was kept in a tube before treating further by chemical means, some photographic experiments were tried. The precipitate was placed on a plate with two objects to be photographed, in a light-tight box. After about three days' exposure a good radiograph resulted, the edge of the mineral where heaped up on the plate being clearly defined all round with an impression of the objects.

Without replacing the precipitate in the tube the experiment was repeated, placing two sheets of brown paper between the mineral and the plate. No result followed, the reason being probably that between the two experiments the precipitate was exposed to the air, and the emanation allowed to escape. I accordingly replaced the precipitate within the tube, corked and sealed it, keeping it in this condition for over four days. At the end of this time the experiment was once again repeated, pouring the mineral out on black paper, the latter being on top of the plate within the light-tight box, and closing the covers of the latter as quickly as possible. The black paper referred to was that used for protection of sensitive plates, and is very opaque to the ordinary rays of light. On development distinct lines of light could be seen on the negative, proving that they had been produced by rays emitted from the precipitate. My reason for keeping the precipitate corked and sealed within a tube for over four days is that it takes about this period of time for a proportion of the emanation to be successively transformed down to radium D, the object being to obtain all three classes of rays, because, as stated before, radium itself, the emanation, and radium A only give out α -rays; radium B is rayless, radium C gives out all three classes of rays, and radium D β -rays and probably γ -rays.

It is therefore these two latter products that are required to ensure good results in physical experiments, and it is clear that if the emanation is allowed to escape these products will not be obtained at all, as the emanation (if I may so use the expression) is the progenitor of them all.

Now, as mentioned above, although the α -rays are present when the concentrates are first extracted, this class of rays is not of great penetrative power; an aluminium plate of only 0.005 centimetre thick is sufficient to decrease the intensity to one-half and a mica sheet 0.01 centimetre thick is sufficient to absorb all the α -rays.

Now, aluminium is not so opaque as most of the other metals, certainly nothing like so much as either iron or titanium; the latter metals being therefore combined with the radio-active matter in the concentrates absorb these α -rays, and in the majority of cases prevent the detection of their presence. Their effects can sometimes be made apparent, because if the concentrates, after being exposed to the air, are spread on a photographic plate, on developing the latter, two or three black spots can, as a rule, be seen, showing that there are a few light-giving particles in the mineral whose α -rays are not entirely cut off.

The question as to whether radio-active ore, as found *in situ*, is in the proper condition for obtaining good physical results here arises. From what has already been stated it is evident that this largely depends upon its porosity. Take, for example, pitchblende, the European ore in which radium is found; this would be classed in common language as a hard rock of close grain. Whatever emanation is therefore produced by any radium that may happen to be present would be occluded within the pores and interstices of the rock, and it would be here transformed continuously and successively into the various products, radium A, B, C, and so on. It must also be remembered that the uranium in pitchblende, before it reaches its final state which is rayless, is transformed into uranium X, which emits β -rays and γ -rays, whilst uranium itself gives out α -rays. There are therefore present all three classes of rays from this source alone, and ore of this character is therefore, with whatever radium its products and other radio-active substances that may happen to be present, in a condition which will produce good results from physical experiments.

On the other hand, taking the concentrates described in this paper as an example, and which, so far as I can discover, contain only one radio-active substance, i.e., radium, these are not in a condition for obtaining good results by physical means when first extracted. The ore where found *in situ* is of a porous character, the ilmenite and rutile in which the radio-active matter is combined being mechanically and somewhat loosely intermingled with silica. Whatever emanation is therefore produced by the radium filters through the silica, is dissipated in the air, and therefore a large proportion of the succeeding products from the emanation is lost.

It may be argued that a large proportion of these products should remain in the ore, as when the emanation filters through the silica a certain amount would cling to each particle, covering it with an invisible film of radio-active matter. This I venture to think is correct; but, on the other hand, most of this product would be washed away during the process of concentration.

Ore, therefore, of this character when extracted is not at first in a good condition for obtaining definite results by ordinary physical means, and it clearly follows that whereas one class of ore in the quantity of radium contained may be richer than another, the same may be poorer in the quantity of the products of radium than the other owing to its greater porosity. It is for the above reasons that it is necessary that the concentrates should be kept within a closed vessel after extraction for the purpose of obtaining results by ordinary physical means, and I opine it was owing to the lack of taking this precaution that other investigators to whom I sent samples failed to obtain results, which I would add, however, is altogether excusable, as the finding of radium under the conditions described is altogether a new occurrence.

The fact that the concentrates were placed in bottles when extracted was a fortuitous circumstance, and if this had not been done the discovery would probably not have been followed up or this paper written, as of course it was necessary to obtain confirmatory results by more means than one.

Having obtained, therefore, good results from precipitate B by photographic means, experiments were made with this and No. 2 precipitate for the purpose of extracting if possible the radio-active matter therefrom.

Finding that Professor Rutherford had extracted radium from thorium and actinium solutions by adding a soluble barium salt and then precipitating as sulphate, and that Madame Curie had stated that radium always follows this element in its reactions, I dissolved precipitate 2 in dilute sulphuric acid, and added barium nitrate which had been dissolved in distilled water. The barium was precipitated as sulphate, the solution was filtered off, and on testing the barium (precipitate 5) I found it to be highly radio-active, more so than the original precipitate 2.

I made several successive precipitations with barium, but found all these latter to be non-radio-active, all the radio-active matter having apparently combined with the barium in the first precipitate. The filtrate was then evaporated down, leaving behind a residue (precipitate 6) which was very slightly radio-active. This radio-activity is probably caused by the products of radium brought down in a similar manner to the quantity brought down with the carbonate of soda (precipitate 4 and precipitate D) in the original tests; the radio-activity was not so great as that of precipitate 4 or precipitate D, as it represents only that of the products formed during the time intervening between the first and second tests.

The quantity of matter as represented by precipitate 2 was small and the quantity of barium (precipitate 5) was not much smaller; the improved radio-activity therefore was brought about not so much by the reduction in bulk of the matrix of the radio-active matter, but by the fact that the opaqueness of barium is not so great as that of the original matrices of titanium and iron.

The fact that the radio-active matter combines so readily with barium is a proof (or at least an indirect one) that radium is present; it certainly is not thorium or actinium, as these elements do not chemically combine with barium.

Precipitate B was then treated in a similar manner, with the exception that I used hydrochloric acid instead of sulphuric; the barium (precipitate E) readily combined with the radio-active matter, and the solution was finally evaporated down, leaving behind precipitate F. The latter precipitate I found to be more radio-active than precipitate 6, resulting doubtless from the products of the emanation brought down from a larger quantity treated than in the previous test. Precipitate E was more radio-active than any sample obtained up to the present time, and it was placed in a corked tube and sealed.

An important point to note in connection with these experiments is that whilst barium will readily combine with the radium, it does not appear to do so with the products of the emanation; the latter come down with the final precipitates after the solution is evaporated, the activity of the same decaying in a similar manner to that of precipitates 4 and D. I have not attempted to separate the radio-active matter from the barium, as the total quantity brought down is somewhat small; in fact, it represents that extracted from only 1 lb. of concentrates. I shall endeavour to do so when the quantity brought down is greater from a larger quantity of the raw material.

The process of separating radium from barium by fractional crystallisation is somewhat lengthy and tedious, and therefore it cannot be stated that adding barium for the radio-active matter to combine with is the best method to be adopted when working on a large scale. Professor and Madame Curie were obliged to adopt this method, as barium already combined with radium exists in pitchblende, whereas in my case this substance was added, as none was found in the crude ore. If something else can be found which will combine with radium and be more easily extracted from it, it will be advantageous. If the method of adding barium has to be adopted, the whole process can be materially shortened by adding the barium nitrate solution instead of the ammonium hydrate to the original solution, and thus the radio-active matter can be immediately extracted with the barium.

Further experiments go to prove that the radio-active matter discovered is radium, as in addition to those already detailed in this paper, I have tried others with thorium,

euxenite, monazite, and other radio-active substances, and find that none, with the exception of radium, correspond with the results obtained; at the same time, until the radio-active matter has been actually extracted from the barium, I suppose I should not state finally that it is radium, as some of my hearers will probably think that the old adage "Seeing is believing" perhaps applies in this case.

The work so far completed may seem to have been somewhat arduous and lengthy, but it has been nothing compared to that of the pioneers in the investigation of radio-active substances. I allude, of course, to the work of Madame and Professor Curie, who, after overcoming great difficulties, brought forward to the view of a wondering world the element known as "Radium."

I should also add that since the first portion of this paper was written, results have been obtained by a metallurgist in Europe who thinks that from the small sample sent the same may be due to the presence of thoria. I, however, reiterate that I think it is due to the presence of radium, having regard also to the nature of the origin of the deposit which I shall now proceed to describe.

Some time after the discovery had been made of the radio-matter in the alluvium, I proceeded again to that part of the country for the express purpose of endeavouring to find out the source from which it was derived. After tracing the course of the alluvium for over 40 miles in length, it came to a sudden termination in a valley or kloof, surrounded on the three sides by kopjes of Waterberg sandstone, the source being what appears to be an extinct mud pipe or vent, similar in many respects, and dissimilar in others, to those that form the well-known diamond mines of South Africa.

The exact spot appears to be clearly defined, as although the usual trees of the bush veldt, consisting principally of the Syringa and Boekenhout type, grow in profusion along the slopes of the valley, at the point indicated there is a marked and an entire absence of these trees, shrubs, or grass. I attribute this to the fact that at the crater's mouth the soil consists nearly entirely of dry clay mud mixed with the concentrates before alluded to, whilst lower down on the alluvium there exists silica of coarser grain, which has evidently been derived from the Waterberg sandstone, through which the pipe has intruded, the latter being a better class of soil for the growth of vegetation and trees than the former.

The walls of the pipe cannot be seen, as they are hidden by the mud lava that has completely covered up its mouth. I, however, picked up in a water-course in the vicinity some samples of igneous rocks, from one of which a rock-slide has been made. Examination under the microscope (confirmed by Professor Young) proves it to be dolerite. Two of the other samples procured are hæmatite or specular iron.

These rocks are frequently met with in the vicinity of diamond mines in Griqualand West, and elsewhere; dolerite, somewhat altered and under this condition known as basalt, is usually found on the outer circumference of a diamond pipe in the form of more or less rounded boulders; hæmatite, or specular iron, is, as a rule, disintegrated and mixed with the alluvial soil, giving it its well-known red appearance.

Now, comparing the nature of the concentrates before alluded to with the deposit of a diamond mine, in both are found magnetite and ilmenite (or what the South African diggers usually call carbon); in some diamond mines zircon is also found, and rutile occasionally in small quantities.

The chief point of dissimilarity is the difference in the size of the grain of the constituent parts when comparing the deposit from both sources.

The largest size grain of any particles of the concentrates is not much bigger than from two to three times that of a pin's head, whilst individual pieces of mineral or pebbles from a diamond mine often attain a considerable size; garnets are sometimes found as large as an apple, ilmenite larger than walnuts, whilst even diamonds occasionally astound the world by their great size.

The other point of dissimilarity is the amount of overflow from this pipe, which extends, so far as length is concerned, for over 50 miles, and whilst this extent of overflow has been helped by a river in the neighbourhood depositing the alluvium, yet the amount of mud-lava gushing forth originally from the mouth of the crater must have been very great, as the alluvium with the radio-active matter in it extends on the one side of the river over the distance named without any large breaks, and, similarly, on the other side of the river for a distance of about 30 miles; the width and depth of the alluvium varies according to the contour of the ground (the latter being Waterberg sandstone) over which it has flowed and been deposited, being from a few feet up to 2000 feet in breadth and from a few feet up to 30 feet in thickness.

There are signs that this river, in consequence of carrying this alluvium and depositing it along its banks, has swerved in places from its original course; it is not practically carrying this alluvium now, as it does not run through the pipe, but (as stated before) in its neighbourhood, and therefore I do not find any radio-active mineral, beyond traces here and there, in its bed as it exists to-day; the presence of the latter commences some distance from the edges of its banks over the dimensions already given, so that the alluvium at present in the bed of the river is pure silica and iron oxide derived from the Waterberg sandstone.

The radio-active alluvium has been found by fire assay to contain traces of gold, but this has evidently been derived from the Waterberg sandstone over which it has flowed, as this metal has been proved to exist in this stratum in quantities from traces up to a half pennyweight to the ton.

Now, I do not know of any diamantiferous pipe that has overflowed to anything like this extent. The pipes forming the Kimberley group of mines have not done so at all. Some of those in the Orange River Colony have overflowed compared with the above to a slight extent, as what are called yellow leads containing diamonds have been found in the alluvial soil some distance away from the pipe, and which I believe in some instances have led to the discovery of the latter. The Premier Mine in the Transvaal has perhaps also overflowed to a slight extent, although I think the deposit found in the neighbourhood is perhaps more due to its having been carried there by a strong spring that rises in the mine and runs through a portion of it. The fact that diamonds have been and are now found for some distance along the banks of the Vaal River can hardly be quoted as an example of overflow from the pipe itself, as this river, if it does not to-day run through a diamantiferous pipe, probably did so originally by a course now dried out.

Great as has been the flow before alluded to, it is of course quite insignificant compared with the enormous flows of other igneous lava sheets existing in South Africa. I allude principally to the diabase sheets that cover up thousands of square miles of country, and which have hidden the blanket reefs in the Witwatersrand formation, both on the east and west extensions. None of the pipes or vents through which these enormous flows of lava have issued forth and spread over the strata beneath have yet been found. This, of course, is due to the fact that the same have intruded only through the strata laid in the earlier geological periods, and are therefore antecedent by several ages to those that form the diamond mines of South Africa, as well as the one referred to containing the radio-active lava; there is existing in places an enormous thickness of different strata overlying these diabase sheets, consisting of black reef formation, dolomite, the Pretoria series, Waterberg sandstone, Dwyka conglomerate, the Eccra shales of the Karroo series, and the coal measures, whilst the Kimberley group of mines has extended right up through the Eccra shales of the Karroo system.

These pipes or vents by which the diabase was brought up must be of a purely volcanic nature, but the question arises are diamantiferous pipes, or the one described in

this paper, volcanic or more thermal in their origin? Mr. Gardner Williams, the General Manager of De Beers Consolidated Mines, in his book entitled "The Diamond Mines of South Africa," has expressed the opinion that the pipes forming the diamond mines of South Africa were formed more by thermal than volcanic action. I am of opinion that at least this is so in the case under review, which means that the mud-lava has been brought up from unknown depths, accompanied by thermal waters, vapour, and steam, and has welled over the mouth of the pipe, the comparatively large quantity of alluvium being deposited in the manner before described.

It may be mentioned that the samples with which nearly all my experiments have been done came from a point on the alluvium over 40 miles away from the crater; whether the concentrates in the pipe will be richer in radio-active matter cannot as yet be positively asserted. A small surface sample in my possession does give rather better results. I would, however, here add that should the radio-active lava become more solid in its nature as depth is attained, *i.e.*, more of the nature of blue ground, as found in a diamond pipe, following the line of reason as detailed before in this paper, it should be richer in the products of radium than the ore in the upper levels of the pipe or that comprising the alluvium. The question, however, will soon be decided, as I hope shortly to undertake exploratory work at the source itself.

Assuming that the radio-active matter discovered be radium, it is necessary to say something with regard to its life.

The life of radium, or perhaps I should say "the stability of its atom," has been computed by Professor Rutherford at eight hundred years, *i.e.*, the time taken for radium to be half transformed, whilst its average life is taken at eleven hundred years. These figures have been arrived at by mathematical deduction from experiments made from concentrated radium; I should think, however, that from what has been stated previously, quoting Professor J. J. Thomson, that the life of radium when distributed throughout a mass of ore is somewhat longer than this. It will, however, serve my purpose to quote the above figures as being correct for the life of radium under this condition.

To account for the existence of radium as we now find it, Professor Rutherford has advanced the theory that it is being gradually produced from uranium, the only class of ore in Europe in which it has been found. Professor Ramsay has already practically proved that one of the products of the emanation from radium is helium, which appears in the earlier transformations, *i.e.*, from the emanation to radium A and B; thus the one being a theory resulting from a mathematical deduction of the life of radium and the other a practical proof, are examples of the fulfilment of the dream of ancient philosophers who were constantly endeavouring to change one element into another.

Now, if radium is produced from uranium in European ores, whence comes the radium (assuming this to be the element) in the case under review? I have found no trace of uranium. On the other hand, it is practically certain that the mud lava, as now found *in situ*, was brought up and deposited more than eleven hundred years ago. We know that the Waterberg sandstone, upon which the alluvium rests, and which is a water-borne stratum, and although the most recently formed in the Transvaal (with the exception of the Lebombo Mountains on the border) was laid down more than eleven hundred years ago; in fact, this stratum belongs, in the opinion of geologists, if not to the archæan age, at least to the primary age, as no fossils exist therein. We are also fairly certain that the volcanic or thermal activity of that portion of the earth's crust known as South Africa occurred more than eleven hundred years ago. It is true that the Kimberley group of pipes has intruded into strata (*viz.*, Dwyka conglomerate and Eccra shales, belonging to the Karroo system) of a younger age than the Waterberg sandstone, but in these

also no trace of fossils are found, and are therefore of great age.

It may be an open question whether the igneous rocks forming the pipes referred to were intruded into these various strata before or after the coal measures were laid down. No case exists to my knowledge where one has been intruded into the coal measures, and if a pipe were found under these strata it would the more certainly prove the point; however, it is the opinion of Transvaal geologists that the later volcanic or thermal activity in this part of the world certainly occurred more than 1100 years ago. Whence then is the radium derived, how is it being formed to-day, and when its life of 1100 years is completed what is the final product? To the latter portion of this question I believe no one can with certainty reply, because, as before stated, the final product has yet to be found. With regard to the former portion of the question, as one who is only commencing the study of the subject of radio-activity, I tentatively put forward the suggestion with all diffidence that the radium is being produced from titanium, and that in this case this element has taken the place of uranium in the European ores.

Two objections immediately present themselves to this theory. The first is that the metals in uranium, with which radium is combined, have all been found to be of high atomic weight, and it has been inferred by Professor Rutherford and others that there is some relation between this fact and that some of them are radio-active. The atomic weight of radium is 223.3, of barium is 136.4, of uranium is 236.7; whilst the atomic weight of titanium is very low (viz., 47.7), that of zirconium is somewhat higher, being 89.9.

Is it possible that a gap *now* exists in the sequence of the order of the elements, and that in ages long since gone by there were present a series of these elements whose atomic weights ranged from titanium on the one side in ascending order, and that these elements have been transformed successively from one to the other until, at the present time, that known as radium is the existing product?

This idea is suggested as it apparently coincides with that occupying the minds of all the leading scientific investigators, physicists, and savants of the world.

Sir William Crookes, in his paper entitled "Modern Views on Matter: The Realisation of a Dream," states that "men who devote themselves to science to-day have gone so far as to admit the possibility of resolving the chemical elements into simpler forms of matter, or even of refining them altogether away into ethereal vibrations of electrical energy."

This, in other words, means that everything in Nature is undergoing a change, and that radio-activity is going on all around us, but that in the majority of cases the change is so slow that our senses are not keen enough to perceive it nor our instruments sensitive enough to detect it.

The second objection to this theory is that if radium can be produced from titanium in the one case, why cannot it be in another? Why, for instance, cannot it be produced from the ilmenite (a compound of iron and titanium) which practically exists in varying quantities in every diamond pipe?

I have tested the deposit from several diamond pipes and found no radio-activity contained therein.

A somewhat analogous case perhaps may be cited in that of polonium, which is found in pitchblende. Polonium is radio-active bismuth, and is not so merely by induction from uranium or radium, but is of itself radio-active, and although it gives off no emanation, I have found that it is capable of exciting radio-activity in surrounding objects, thus proving (as stated in the earlier portion of this paper) that this induced radio-activity is not caused only by the emanation (as there is none in this case), but also must be produced by one or more classes of rays that are emitted by the substance itself. Now the ordinary bismuth of commerce is not radio-active, why, then, should the bismuth that is found in pitchblende be radio-active? Is some of the uranium in this case being transformed into

polonium in a similar manner to other portions which are being transformed into radium, and, if so, whence comes the original activity of uranium, i.e., from what element is this being derived?

To these queries and the objections I have raised to the theory that radium is being derived from titanium, I am afraid at the present time I cannot adequately reply, nor can I give any alternative theory. The whole subject of radio-activity has recently been likened by one professor to "a mountain whose peak is hidden in the clouds of heaven, and on whose slopes men still are struggling." I have been struggling on one of the lowermost slopes, but I trust by the time this investigation is completed to have risen to a higher level.

We have, however, the advantage to-day of having amongst us some of those great scientific investigators who have made the subject of radio-activity a special study, and who (to use the simile I have just referred to) are rapidly rising towards the peak of the mountain, even if they have not already gained the summit; their remarks, therefore, on some of the points brought forward will be deeply interesting.

TRIBO-LUMINESCENCE IN THE ACRIDINE SERIES.

By GILBERT T. MORGAN.

88-DINAPHTHACRIDINE, $C_{10}H_6$  $C_{10}H_6$, which was

first discovered by Reed (*Journ. Prakt. Chem.*, 1886, xxxv., 314), and subsequently re-examined by the author of this note (*Trans. Chem. Soc.*, 1898, lxxiii., 549), usually crystallises from alcohol in straw-coloured needles, but when allowed to separate very slowly from its solutions in alcohol, ethyl acetate, acetone, or benzene, it is deposited in transparent amber-coloured prisms, which become opaque when heated at about 120° and melt at 216°, having the same melting-point as the acicular crystals. Both forms of the base, when crushed between two ground-glass covers such as are used in closing gas-jars, emit a vivid yellowish luminescence; the phenomenon continues until the crystals are completely pulverised, and is accordingly more marked in the case of the hard prismatic variety. When the amber-coloured prisms adhere to the sides of the crystallising vessel the luminescence is observed on scraping the crystals with a spatula. This case of tribo-luminescence is of especial interest as being noticed in the case of a coloured substance which in solution also exhibits an intense bluish purple fluorescence.

Tribo-luminescence is not manifested by the yellow hydrochloride, hydriodide, methiodide, and ethiodide of $\beta\beta$ -dinaphthacridine, and the simplest base of the series—namely, acridine itself—does not exhibit this property when scratched or pulverised in the manner indicated.

Royal Institution.—A Christmas Course of Lectures (adapted to a Juvenile Auditory) will be delivered at the Royal Institution by Professor Herbert Hall Turner, D.Sc., F.R.S., on "Astronomy." The dates of the Lectures are December 28, 30, 1895, January 2, 4, 6, 9, 1906, at Three o'clock.

Awards at the Liège International Exhibition.—The international Jury of the Liège Exhibition have conferred upon Burroughs, Wellcome, and Co. six Grand Prizes, three Diplomas of Honour, and three Gold Medals for the scientific excellence of their products, including "Wellcome" Brand Chemicals, "Tabloid" and "Soloid" Brand Products, "Kepler" Preparations, "Tabloid" Brand Photographic Chemicals, "Hazeline" Preparations, Pleated Compressed Surgical Dressings, "Tabloid" Brand Medical Equipments, &c.

THE INFLUENCE OF PHASE CHANGES ON THE TENACITY OF DUCTILE METALS AT THE ORDINARY TEMPERATURE AND AT THE BOILING-POINT OF LIQUID AIR.*

By G. T. BEILBY and H. N. BEILBY, B.Sc.

THE observations recorded in this paper are intended to prepare the way for a more direct attack on the problems of molecular cohesion by the establishment of clearer views as to the influence of changes of phase on the tenacity of ductile metals at various temperatures.

According to the phase theory of the hard and soft states in metals which was first developed by one of us more than a year ago, the changes of state from hard to soft and from soft to hard were shown to be due to the changes of phase brought about, in the one case by heat, and in the other by mechanical deformation or flow. In the ductile metals the crystalline is the mechanically unstable phase, while the amorphous only becomes thermally unstable when a definite temperature is reached.

The comparative mechanical instability of the two phases is well illustrated in the stretching of wires under tension. Annealed wires, which are in the C phase, stretch when they are stressed beyond the yield point; hardened wires, which are partly in the A phase, do not stretch—they break without extension when their limit of tenacity is reached.

The homogeneous C phase in ductile metals has no true breaking-point—it yields and stretches when stressed beyond the elastic limit, and in so doing it passes partly into the A phase, and rupture occurs at the breaking point of the mixed structure. The tenacity of the mixed structure approaches, but never quite reaches, that of the homogeneous A phase. For the purpose we had in view it was necessary to obtain the metals as nearly as possible in this homogeneous condition.

Wire drawing was the means employed for the breaking down of the C phase. After a wire had been stretched to four or five times its original length by drawing it through the holes of a wire plate, all the ordinary traces of crystalline structure disappear, but it still consists of minute granules of the C phase embedded in a matrix of the A phase. Further drawing at the same temperature alters the mixed structure only slightly; for each temperature there appears to be a certain mechanical equilibrium between the phases. By lowering the temperature of drawing, the C phase is further broken down into still smaller granules, and the mixture approaches more nearly to the homogeneous A state.

Our observations were made on wires which had been as completely as possible converted into the A phase by wire drawing at the ordinary temperature, and in every case the tenacity observed was higher than any which has been recorded by previous observers for equally pure metals.

Gold (Purity, 9997 per 10,000).

Tenacity at 288° abs. (15° C.) . . 15.6 tons per sq. inch.
" 53° " (-180° C.) . 22.4 " "

Silver (Purity, 10,000 per 10,000).

Tenacity at 288° abs. (15° C.) . . 25.7 tons per sq. inch.
" 53° " (-180° C.) . 34.4 " "

Copper (Conductivity, 100 per cent).

Tenacity at 288° abs. (15° C.) . . 28.4 tons per sq. inch.
" 53° " (-180° C.) . 36.0 " "

The wires broken at the ordinary temperature showed no general stretching. There was a slight extension of from $\frac{1}{4}$ to 1 per cent, due entirely to a sharp reduction of diameter at the actual point of rupture. At the boiling-point of liquid air all the wires stretched from 11 to 12 per

cent. This stretching was uniform over the whole length between the grips. This was confirmed by exact measurements of the diameter at a number of points.

The appearance of the fractured ends reveals several points of interest. In every case the copper wires showed the cupped formation at the extreme end. This formation is evidently due to the lower tenacity of the central core, due to the presence of gas bubbles which have been drawn out into long tubes or cells. The silver wires occasionally showed a slight cupped formation, but in this case the gas bubbles to which it was due were globular, as if they had been evolved at the moment of fracture. The gold wires were practically free from sponginess, and the fractures were almost perfectly viscous.

By drawing wires at the lowest possible temperatures we hope to obtain the ductile metals in their condition of maximum tenacity, and from the figures then available to be able to calculate the molecular cohesion at the absolute zero.

SOME OBSERVATIONS ON COLUMBIUM.*

By ROY D. HALL and EDGAR F. SMITH.

THE starting-out material in this study was columbite from Lawrence County, South Dakota. Its specific gravity equalled 5.86. It contained 81 per cent of the mixed oxides of columbium and tantalum. The total quantity of substance decomposed by fusion with acid potassium sulphate (58.5 kilogms.) was 21.3 kilogms. Each fusion was made in a platinum dish, using 100 grms. of mineral and 275 grms. of acid potassium sulphate. While still liquid the mass was poured into a porcelain dish. When cold the fusion separated readily from the dish, and was broken into small pieces, which were boiled with water in large No. 11 evaporating dishes until thoroughly disintegrated; when they were transferred to precipitating jars, and the hydrates washed by decantation until the wash-water gave no precipitate or only a slight precipitate with ammonium hydroxide. The solution and the washings were evaporated to dryness. The residue was designated Part I. The moist hydrates of columbium and tantalum were covered with ammonium sulphide, and allowed to stand for several days. This ammonium sulphide solution was decanted and designated Part II. The remaining oxides were finally treated with very dilute sulphuric acid, and then thoroughly washed with water. The washings and the diluted sulphuric acid solution were also evaporated to dryness, and marked Part III. The residue labelled Part I. contained potassium and the bases from the mineral in the form of sulphates. It was dissolved in water, poured into five-gallon jars, and there precipitated with a slight excess of ammonium hydroxide. Having decanted the supernatant liquid the precipitate was washed once with water, after which the hydrates were covered with a solution of ammonium carbonate, and allowed to stand for several days. The ammonium carbonate solution was then syphoned off, acidulated with dilute hydrochloric acid, and any metal present precipitated with a slight excess of ammonium hydroxide. The hydrate obtained in this way was dissolved in dilute hydrochloric acid, and an excess of ammonium carbonate, together with ammonium sulphide, added to its solution. The iron separated in the form of sulphide, and with it there was a small amount of titanium. The filtrate from this precipitate was boiled with hydrochloric acid, and ammonium hydroxide added. The hydrate which was precipitated was ignited and tested as to its photographic power. It gave a picture after an exposure of five days. It contained uranium. It showed the greenish colour characteristic of U_3O_8 . After this it was fused with acid potassium sulphate, taken up in water, and the solution boiled. A precipitate formed on cooling,

* Read before the British Association (Section B), South Africa Meeting, 1905.

* Proceedings of the American Philosophical Society, 1905, xlv., p. 177.

but disappeared on warming, thus indicating the presence of members of the cerium group or of zirconium. On the addition of ammonium hydrate there separated a hydrate which, after filtration and washing, dissolved completely in a solution of oxalic acid. This pointed to the presence of zirconium. The hydrates were again precipitated, dissolved in sulphuric acid, and the solution neutralised with potassium carbonate, and saturated in the cold with potassium sulphate. By this precipitation the zirconium was obtained in the form of insoluble double sulphate, while the uranium remained in solution. After filtering out the zirconium potassium sulphate it was dissolved in hydrochloric acid, and zirconium hydrate precipitated with ammonium hydroxide. It was well washed with water, and dissolved in hydrofluoric acid. An equivalent amount of potassium carbonate was added, and, on evaporation, potassium zirconium fluoride crystallised out. Three grms. of this salt were obtained.

Analysis.—0.5043 gm. of the salt ignited with sulphuric acid gave 0.5272 gm. of $K_2SO_4 + ZrO_2$, and contained 0.2212 gm. of ZrO_2 , leaving 0.3060 gm. of K_2SO_4 .

	Calculated, K_2ZrF_6 .	Found.
2KF	41.05	40.47
ZrF ₄	58.95	59.52
	100.00	99.99

The uranium in the filtrate from the zirconium was precipitated with ammonium hydroxide, dissolved in hydrochloric acid, and an excess of sodium hydroxide added to this to obtain the glucinum. This was not found. The uranium was changed to nitrate, and the solution allowed to evaporate, when large characteristic crystals of uranium nitrate separated. The solution decanted from the original ammonium hydroxide precipitate, which contained manganese and allied elements, was treated with an excess of sodium carbonate. The precipitate produced was allowed to settle, the supernatant liquid decanted into other jars, and hydrogen sulphide passed through it. A small amount of a black sulphide was obtained. It consisted of zinc, iron, copper, and nickel (from the crucible tongs). The precipitate produced by sodium carbonate contained manganese, zinc, and iron. Ten grms. of it were dissolved in hydrochloric acid, and the iron removed by the basic acetate method. The zinc was then precipitated as sulphide. The latter was changed to chloride, and tested for gallium. Not a trace of the latter was found. Zinc lines alone were shown in the spectrum.

Tin and tungsten were contained in Part II. Part III. was not further examined. It may be concluded therefore that the columbite from South Dakota contains as acids—tantalum, columbium, titanium, silicon, zirconium, tin, and tungsten; as bases—iron, manganese, zinc, uranium, copper (?), and nickel (?).

The moist metallic acids, after having been washed with dilute sulphuric acid, were brought into a large platinum dish, and dissolved in fairly concentrated hydrofluoric acid. This solution was then filtered, through a hot water funnel, from undecomposed mineral, and from potassium silicofluoride (due to the presence of some potassium sulphate in the moist oxides). The hydrofluoric acid solutions were collected in large rubber dishes, and sufficient potassium hydroxide was introduced to convert the tantalum into potassium tantalum fluoride, most of which separated out and was removed by filtration. This precipitate was dried as far as possible by suction. It was washed once, and then allowed to dry in the air. It weighed 11 kilograms. The mother-liquor from the potassium tantalum fluoride was evaporated in stages, potassium hydrate being added. The columbium separated usually in hexagonal, hard, short crystals, such as separate from a strongly acid solution containing an insufficient amount of potassium fluoride. The total residue obtained in this way amounted to about 8 to 10 kilograms. These residues were decomposed by treating them with twice their own

weight of sulphuric acid, heating gently until the bulk of the hydrofluoric acid was expelled, and then evaporating until the mass fumed strongly, and maintaining the temperature until the excess of sulphuric acid had been almost completely driven out. Several hours were required for this. It is necessary in order to get rid of the hydrofluoric acid. The residual mass was boiled with water to extract the bases which dissolved as sulphates. The insoluble hydroxides were thoroughly washed and dissolved in hydrofluoric acid. The first crop of crystals, obtained by evaporation with potassium hydroxide, was removed, and the mother-liquor then evaporated to dryness with sufficient potassium hydroxide to change all of the metallic acids into double fluorides. A portion of these crystals (first crop) was dissolved in water, and the tantalum removed by adding dilute potassium hydroxide to the solution, which, after the formation of a permanent precipitate, was boiled for some time. The precipitate consisted mainly of potassium tantalum oxyfluoride. It was filtered out, and the filtrate evaporated to dryness. The residue was baked for some time at 200°. By this procedure some hydrofluoric acid was expelled, and, on taking up the residue with water and boiling, more potassium tantalum oxyfluoride separated. By repetition of this process all of the tantalum was removed from the solution. The only test relied upon for the detection of tantalum was the solution of this precipitate in a drop of hydrofluoric acid and evaporation to crystallisation. If needles separated their solubility in water was used to ascertain whether they were potassium tantalum fluoride or potassium columbium oxyfluoride. It is true that this test consumes considerable time, yet it is the only satisfactory means of determining with which of the metals the chemist is dealing. The formation of a precipitate by protracted boiling of a dilute solution of potassium tantalum fluoride is not conclusive, for Krüss and Nilson (*Ber.*, 1881, 1676) have shown that potassium columbium oxyfluoride deposits under like conditions a small amount of a salt containing less fluorine. Further, the double fluoride must be re-crystallised several times, so that it will be sufficiently free from acid that tantalum, if it is present in small amounts, may be precipitated by boiling.

Having freed the double fluoride from tantalum, it was dissolved in water and hydrogen sulphide conducted through its solution. A slight precipitate of platinum sulphide was obtained. The filtrate from it was evaporated to dryness and the residue baked. On dissolving in water more platinum sulphide was found, but when hydrogen sulphide was conducted through the filtrate no further precipitation took place. The first crop of crystals got by the evaporation of this solution showed the usual form of potassium columbium oxyfluoride. They were allowed to dry in the air and labelled crystals No. 1 (A). The filtrate from them was reduced to a small bulk. Strong hydrofluoric acid was added when the needles of potassium columbium fluoride (K_2Cbf_7) separated. These were dried between bibulous paper and labelled crystals No. 2 (B). Samples from these two crops of crystals were analysed.

Analysis of No. 1 (A).

0.53 gm. of salt gave 0.2346 gm. of oxide and 0.3161 gm. of potassium sulphate.

$$0.2346 : 0.3161 :: x/2 : 174 \quad x = R_2O_5 = 258.2.$$

	Calculated, $K_2Cbf_7H_2O$.	Found.
K_2SO_4	57.81	59.64
Oxide	44.52	44.26

The crucible in which the ignition of oxide occurred was stained. This was undoubtedly due to the presence of tin, which had not been removed, although hydrogen sulphide had been conducted through the solution of the double fluoride.

Analysis of No. 2 (B).

0.8428 gm. of salt gave 0.3635 gm. of oxide and 0.4803 gm. of potassium sulphate.

0.4811 grm. of salt gave 0.2082 grm. of oxide and 0.2775 grm. of potassium sulphate.

0.3635 : 0.4803 :: $x/2$: 174 $x = 263.4$.

0.2082 : 0.2775 :: $x/2$: 174 $x = 250.1$.

	Calculated, $K_2C_2F_7$.	Found.	Found.
K_2SO_4	57.05	56.99	57.68
Oxide	43.93	43.13	43.28

Specific gravity of oxide (B) :—

18.5924 pycnometer + water, $t = 18^\circ$

0.2346 grm. of oxide taken

18.8270

18.7760 pycnometer + water + oxide 0.2346

0.0510 grm. water displaced 0.0510 4.60 sp. gr.

To determine the titanium content of the columbium oxide recourse was had to a comparison of the colour tint produced by hydrogen peroxide in an oxalate solution against known amounts of titanium hydrate dissolved in oxalic acid. Thus, 0.2262 grm. of columbium oxide was fused with acid potassium sulphate and the fusion dissolved in oxalic acid and diluted to 50 c.c. It gave a colour equivalent to 0.4 c.c. of the standard titanium solution (1 c.c. contained 0.00006 grm. of titanium dioxide). In other words, by this test the columbium oxide was thought to contain 0.000424 grm. of titanium dioxide, or 0.18 per cent.

Solubility of Crystals A.

One part of the salt was found to be soluble in a little over twelve parts of water. This is the solubility of potassium-columbium oxyfluoride.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, October 27th, 1905.

Prof. J. H. POYNTING, F.R.S., President, in the Chair.

A PAPER ON "The Theory of Phasemeters" was read by Dr. W. E. SUMPNER.

Phasemeters are instruments of the dynamometer type for indicating the phase relations of the currents and potentials in alternating-current circuits. With few exceptions, they are made for use on multiphase circuits. Such instruments consist essentially of two sets of coils, of which one set is fixed, and the other forms a single moving system which is not provided with any form of control. The currents in one set of coils are determined by the voltages of the main circuits; while those in the other set are produced by the circuit currents. With rare exceptions the magnetic circuits of phasemeters are air-circuits, containing no iron, so that the magnetic fields associated with them are weak, and the instruments in consequence are of somewhat delicate construction. There, however, appears to be no reason why the use of iron should be avoided in these instruments, and the author shows in the paper that the theory of the instruments is the same whether they contain iron or not, and however the coils may be arranged; that they can be calibrated by direct current methods, although for use on alternating current circuits; and that a new type of instrument, containing iron, conforms to the theory given. In all the cases considered, it is assumed (1) that the induction density at any point due

to the current A in a fixed coil is represented by AF , where A is the instantaneous value of the current A , and F is a quantity dependent merely on the coil and the position of the point considered; and (2) that the principle of superposition holds, viz., $B = A_1F_1 + A_2F_2 + A_3F_3$, where A_1, A_2, A_3 are the currents in the three fixed coils, and the quantities F are functions of the position of the point corresponding to these fixed coils. The author shows that these assumptions hold good even when the path of the lines of force lies partly through (suitably laminated) iron and it is necessary to consider the effect of varying permeability and hysteresis. The main results of the investigation are :—

1. Phasemeters for multi-phase circuits are all equally accurate on balanced loads provided they have been correctly calibrated and possess no faults due to purely mechanical causes. Their accuracy is not affected by variations in wave-form or in current-frequency. The calibration of the scale is affected by the number of coils used in the instrument, by the ratios of the ampère-turns used with these coils, by the distribution of the windings, and by the magnetic nature and properties of the magnetic circuits, especially if these contain iron; but the accuracy of the indications is not dependent upon any of these considerations, if the working of the instrument is satisfactory from a mechanical point of view.

2. Phasemeters can be simply and accurately calibrated for balanced loads by means of a direct-current method of test.

3. The error of phasemeters on unbalanced circuits is generally serious for loads which are badly out of balance. The error, like that of a wattmeter, increases rapidly as the power-factor of the load diminishes. It can only be reduced at the expense of complication in the instrument, by increasing the number of coils used in the fixed and moving systems, and by arranging the coils and magnetic circuits to be symmetrical in regard to one another. If the true power-factor of the load is $\cos\phi$, the reading of the instrument is—

$$\cos\phi + \theta \sin\phi,$$

where θ is the phase error due to the unbalanced load, and is the product of two factors, one of which is the maximum value of θ determined by the amount the load is out of balance, and the other may have any value between $+1$ and -1 and determines whether the instrument reads high or low.

The Secretary read a letter from Mr. A. RUSSELL referring to one of the fundamental assumptions made by Dr. Sumpner. The magnetic force B , at any point on the conductor of the moving coil had been represented by $A_1F_1 + A_2F_2 + A_3F_3$, where F_1, F_2 , and F_3 were considered constant. The instantaneous value of the magnetic force at any point was the resultant of the three magnetic forces k_1A_1, k_2A_2 , and k_3A_3 , acting in fixed directions at that point. At any instant therefore—

$$B = k_1A_1 \cos\phi_1 + k_2A_2 \cos\phi_2 + k_3A_3 \cos\phi_3,$$

where ϕ_1, ϕ_2 , and ϕ_3 are the angles between B and k_1A_1, k_2A_2 , and k_3A_3 . As A_1, A_2 , and A_3 are not in phase with one another, the direction of the resultant magnetic force is continually altering, and thus ϕ_1, ϕ_2 , and ϕ_3 are functions of the time. Hence, also, the author's factors F_1, F_2 , and F_3 are not constants, but functions of the time, and thus the conclusions arrived at in the paper must be modified. Dr. Sumpner's method of calibrating by means of direct currents was novel and valuable, but little confidence could be placed in the readings of phasemeters when the applied waves of potential difference did not follow the harmonic law.

Mr. A. CAMPBELL, referring to the stepped nature of one of the calibration curves obtained by the author, asked if the use of a smooth core instead of a channelled one would result in a smoother curve.

Mr. K. EDGECUMBE expressed his interest in the paper, and said it was valuable because phasemeters were coming

* Probably too high because it was not heated enough to expel all of the sulphuric acid.

into general use, and the literature on the subject was small. Dr. Sumpner had stated in his paper that previous theories had neglected the question of the currents being unbalanced, but he pointed out that Punga in 1902 had described power-factor indicators, and showed how they could be used with unbalanced loads. It was important to define exactly what is meant by average power-factor. The author had given a mathematical definition, but a simpler definition would be that the average power-factor is that quantity which multiplied by the phase-voltage and the sum of the three currents gives the total power supplied to the line. A disadvantage of power-factor indicators was the difficulty of testing them.

Mr. W. DUDELL asked if the author had assumed that the three voltages were in symmetrical phase relation, and pointed out that in practice differences of as much as 10° might occur.

Dr. SUMPNER, in reply, said that in the proof of the paper B was not the *maximum* flux but the effective part of it, that at right angles to the direction of motion of the conductor. He was aware that it was possible to obtain smoother curves, and had partially done it by a suitable distribution of winding giving a gradually varying flux. In reply to Mr. Duddell, he said he had assumed equal voltages and equal phase relations.

Prof. H. L. CALLENDAR described an Apparatus designed for Measuring the Coronal Radiation during an Eclipse.

The coronal radiation was received by a mirror with an aperture of 20 inches and a focal length of 45 inches, giving an image of the sun approximately 1 c.m. in diameter. The instrument was mounted equatorially, and was provided with a diagonal flat which projected the image to the side of the tube in a convenient position for observation with an eyepiece or a sensitive bolometer or thermopile. The tube of the telescope was fitted with a diaphragm of 15 inches diameter, which limited the aperture considerably but improved the definition. With this reduction, after allowing for obstruction by the flat, and for loss at the two reflections, the effective concentration of the rays at the focus was upwards of 1000 times. The absolute recording bolometer was designed for the determination of solar radiation in absolute measure by the electric compensation method. The radiation admitted through a measured aperture of 3 sq. c.m. was received on a blackened grid of fine platinum strips arranged in such a way as to intercept the whole of the admitted radiation. The increase of resistance of the grid was automatically recorded by means of a Callendar recorder of the usual pattern. The intensity in absolute measure was determined by observing the value of the electric current required to produce the same rise of temperature in the grid as the radiation to be measured. The apparatus was mounted on the tube of the 20 in. reflector, and the openings in the roof of the hut were arranged to permit of continuous records being taken between the hours of 10 A.M. and 3 P.M., so as to include the whole duration of the eclipse. Apart from its use for recording the variations of solar radiation, the instrument was intended for reducing to absolute measure the readings of the coronal thermopile. The coronal thermopile designed for the 20 in. reflector had a receiving surface consisting of ten small rectangles of very thin copper arranged in the circumference of a circle nearly fitting the image of the sun, so as to receive the greater part of the radiation of the inner corona. The copper rectangles formed the inner junctions of a series of thin bars of antimony and bismuth alloys arranged radially on a very thin supporting disc of mica. The outer ends of the couples were connected by thin copper strips at the outer circumference of the mica disc. The pile was constructed in two halves of five couples each on opposite sides of the disc, and the two halves were connected either in series or opposition through a suitable switch to the galvanometer. The mica disc carrying the thermopile was suspended in an ebonite ring by means of four thin connecting wires

attached to terminals fixed in the ring. The ebonite ring carried on one side a tube sliding in the eyepiece fitting by which the plane of the thermopile could be adjusted to coincide with the focal plane of the mirror, and on the other side a thick metal tube with diaphragms to screen the thermopile from draughts and from extraneous radiation. The galvanometer employed was of the movable-coil type, with a plane mirror 1 inch in diameter reflecting the image of a transparent millimetre-scale at a distance of 3 metres into a telescope of 2 in. aperture and 3 ft. focal length. The suspension was of very fine phosphor-bronze, giving a deflection of 5 c.m. for one microvolt with the thermocouple in circuit. In taking observations with the thermopile, it was possible either (1) to read the deflection of the galvanometer, or (2) to compensate the galvanometer deflection by introducing an opposing E.M.F. of known value into the circuit. A preliminary test of the apparatus with the thermopile directly exposed to radiation of known intensity, showed a deflection of nearly 25 c.m. for one-thousandth of a calorie per sq. c.m. per min., so that radiation one-millionth of full sunshine could be detected with certainty without using a mirror. When placed in the focus of the telescope, radiation one-thousand times smaller than this could be observed, so that even if the intrinsic heat-radiating power of the corona were only one ten-millionth of the solar surface it could still be measured to within 1 per cent. The essential point in the observations was to eliminate the variable effects of atmospheric radiation, for which a differential method of observation with the two halves of the pile was particularly suitable. In taking observations on the corona, the motion of the moon during totality was made use of to define the exact area of the corona corresponding to the differential reading. At the commencement of totality, the thermopile being centred on the sun, the inner corona on the eastern limb would be fully exposed, while on the western it would be partly covered by the moon. At the end of totality the reverse would be the case. The difference of the readings would correspond to the radiation of the strip of the inner corona uncovered by the motion of the moon between the two readings. The area of the strip of corona considered could be accurately determined from the times at which the readings were taken.

Mr. SLATER asked if, in the method employed by Prof. Callendar for getting rid of atmospheric radiation, he had assumed that the corona was symmetrical and that there were no prominences.

Prof. CALLENDAR said he did not think it was possible to distinguish between the radiation from the corona and that from prominences. The method he had employed did not depend upon the symmetry of the corona.

NOTICES OF BOOKS.

Select Methods in Chemical Analysis. By Sir WILLIAM CROOKES, Hon. D.Sc. (Oxford and Dublin), F.R.S., P.P.C.S., P.P.Inst.E.E. Fourth Edition, Re-written and Enlarged. London, New York, and Bombay: Longmans, Green, and Co. 1905.

THE fourth edition of this work gives a complete account of the author's experience regarding the application of analytical processes to the elements and their compounds, their detection in minerals and ores, their extraction from various sources, and rapid methods of estimation suitable for use for commercial purposes, as well as more exact methods to be employed when extreme accuracy is a desideratum. The preparation and separation of the rare earths are included, together with an account of the most recent work that has been done on this subject. A chapter on Electrolytic Analysis and Gas Analysis describes the most accurate and convenient methods now in use, while another chapter is devoted to the consideration of miscel-

laneous processes, new methods and apparatus, and many special devices for economising time without sacrificing accuracy, as for example, in the shortening of filtering operations. The correct adjustment of weights, which is a subject often overlooked even when the highest degree of accuracy is desirable, as in the determination of atomic weights, is described fully, and tables are given for the mutual conversion of the decimal and English systems of weights and measures.

Researches on the Affinities of the Elements, and on the Causes of the Chemical Similarity or Dissimilarity of Elements and Compounds. By GEOFFREY MARTIN, B.Sc. (Lond.). London: J. and A. Churchill. 1905.

THIS work represents one of the first attempts to discover the relationships existing between chemical properties and atomic weight. For this purpose the author has investigated a great number of compounds, and has found that the affinities of the elements follow a definite "wave law," which he illustrates graphically by the construction of diagrams called affinity surfaces. These are made by plotting the positions of the elements according to the Periodic System on a plane surface, and erecting the perpendiculars through the point corresponding to each element, proportional to the attractive force which it exerts on the atoms of various other elements; the affinity surface is then the surface containing all the end points of these perpendiculars. Each element has a characteristic surface of its own, and allied elements have similar surfaces. One important conclusion among many others which the author draws from his work is that chemically similar elements attract the same radicles or atoms with proportional intensities of force. A vast amount of work must have been done in collecting the data for the book, and the author displays considerable originality of thought and ingenuity in arranging his facts, detecting relationships, and drawing conclusions, which make his book a valuable contribution to chemical literature. Some portions of it have already been published in a series of articles in the CHEMICAL NEWS, in which an abstract of the wave law and summaries of some of the important points in the argument were given.

A Three Years' Course of Practical Chemistry. By GEORGE H. MARTIN, M.A., F.C.S., and ELLIS JONES, M.A. First and Second Year. London: Rivingtons. 1905.

THESE two volumes provide a thoroughly satisfactory scheme for two years' work in elementary practical chemistry, and by the time the student has performed all the experiments and filled in the spaces in the book left for the description of processes and the drawing of conclusions, he will have prepared for himself a complete text-book of chemistry, containing his own experimental results. The preparation of the scheme has evidently been the work of teachers who are skilled in deciding exactly how best to draw out a boy's natural powers and to make his work interesting to him, and the students who use the book should become quite at home in all simple experimental manipulations, besides acquiring a very fair foundation for the knowledge of the principles of chemistry. While some parts of the authors' plan do not seem to be quite unexceptionable, the books will undoubtedly be found of real value, both by teachers and learners.

Die Elektrochemie der Organischen Verbindungen. ("The Electro-chemistry of the Organic Compounds"). By Dr. WALTHER LÖB. Third Edition. Halle-a.-S.: Wilhelm Knapp. 1905.

THESE two volumes the third edition of the author's treatise on the electrolysis and the electro-synthesis of organic sub-

stances, which has been enlarged to such an extent as to necessitate a change of title. The subject matter has been re-written and re-arranged, so that the book now gives a complete survey of the application of electrolytic processes in the region of organic chemistry, and a discussion of methods and appliances used in electro-chemical research, while considerable space is allotted to the consideration of electro-thermic processes and of the silent electric discharge, the last subject being treated in a specially stimulating manner. The author considers his subject both from the practical and theoretical points of view, and describes fully the methods applied, the apparatus used, and the results obtained when electrical energy is employed used to bring about organic reactions.

Engineering Chemistry: a Manual of Quantitative Chemical Analysis. Third Edition. By THOMAS B. STILLMAN, M.Sc., Ph.D. Easton, Pa.: Chemical Publishing Co. 1905.

THE most important additions contained in the third edition of this work relate to the composition, commercial uses, and analysis of asphalt, the examination of lubricating oils and Portland cement, and the technology of the products of the blast-furnace. Besides the addition of this new matter, the whole of the text has been revised in accordance with our latest knowledge of the most rapid and accurate methods of quantitative technical analysis, and for use as a work of reference the book will be found to contain in a compressed form a large amount of information regarding general technical analysis.

CORRESPONDENCE

THE CHEMICAL CONDITIONS OF ELEMENTS.

To the Editor of the Chemical News.

SIR,—Just as in geometry there exists to every theorem concerning lines another theorem where the lines are replaced by points, so, also, in chemistry there exists to every theorem concerning the molecular state of matter another theorem concerning the sub-atomic state of matter. For example, there exist three states of matter of a molecular scale of magnitude—namely, the solid, liquid, and gaseous states; so, also, there exist three states of matter of a sub-atomic scale of magnitude—namely, the non-metallic, metallic, and radio-active states of matter.

In the non-metallic state the electrons oscillate about fixed centres in the body (compare the solid state, in which the molecules oscillate about fixed centres). In the metallic state the electrons are not confined to fixed centres in the body, but possess a freedom of movement within the limits of the body (compare the liquid state, in which the molecules move freely within the liquid, but do not travel outside its limits). In the radio-active state the electrons travel about in all directions, and are not confined to the limits of the body (compare the gaseous state, in which the molecules are not confined to the limits of the body, but travel about in all directions).

Just as any influence which steadily increases the motion of the molecules causes a body to steadily pass successively through the three molecular states—viz., the solid, liquid, and gaseous states—so, also, any influence which steadily increases the motion of the electrons within a body also probably causes it to pass from the non-metallic to the metallic, and finally into the radio-active condition.

So that the chemical state which a given element finds itself in at ordinary temperatures is probably only a phase or condition which other elements could also assume by suitably altering the external physical conditions under which they are viewed—a conclusion which I had pre-

viously arrived at, but from other considerations (see the writer's work, "Researches on the Affinities of the Elements," pp. 207-240, Churchill, London, 1905; also CHEMICAL NEWS, lxxxiii., 130; lxxxv., 205, 310; lxxxvi., 295; lxxxvii., 74, 162).—I am, &c.,

GEOFFREY MARTIN.

University of Kiel, October 15, 1905.

MISCELLANEOUS.

British Science Guild.—The Inaugural Meeting of this Guild, held at the Mansion House, has had the effect of largely increasing the list of applications for membership. Sir Norman Lockyer desires it to be known that would-be members should apply for particulars to the Honorary Secretary, 16, Pen-y-Wern Road, S.W.

Royal Institution.—A General Monthly Meeting of the members of the Royal Institution was held on the 6th inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President in the Chair. Lady Alford, Mr. W. Friedlander, Dr. A. Muirhead, and Mr. D. A. Thomson were elected Members. The Special Thanks of the Members were returned to Mr. Robert Hannah for his gift of the picture, painted by him, of "Master Isaac Newton in his Garden at Woolsthorpe, in the Autumn of 1665."

Appointments.—Dr. Alexander McKenzie, M.A., D.Sc. (St. Andrews), Ph.D. (Berlin), Lecturer and Senior Demonstrator in the University of Birmingham, has been appointed Head of the Chemical Department at the Birkbeck College in succession to Dr. John E. Mackenzie, D.Sc. (Edinburgh), Ph.D. (Strassbourg), who has accepted the appointment of Principal of the Technical Institute, Bombay.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Saccharin.—I am desirous of ascertaining particulars of the manufacture of saccharine (süsstoffe), and whether that chemical is being manufactured in England in a liquid form.—M. C.

MEETINGS FOR THE WEEK.

WEDNESDAY, 15th.—Microscopical, 8. Exhibition of Microscope Slides of Tsetse Fly Dissections, Trypanosomes, &c.

Society of Arts, 8. Inaugural Address of the 152d Session, by Sir Owen Roberts, M.A.

THURSDAY, 16th.—Chemical, 8.30. "Silicon Researches—Part IX. Bromination of Silico-phenyl Imide and Amide, and formation of a Compound including (SiN)—" by J. E. Reynolds. "Condensation of Ketones with Mercury Cyanide," by J. E. Marsb and R. de J. F. Struthers. "Application of the Microscopic Method of Molecular Weight Determination to High-boiling Solvents," by G. Barger and A. J. Ewins. "Green Compounds of Cobalt produced by Oxidising Agents," by R. G. Durrant. "Synthesis of Tertiary Menthol and of Inactive Menthone," by W. H. Perkin, jun. "Optically Active Reduced Naphthoic Acids—Part I. Dextro- Δ^2 or 3-dihydro-1-naphthoic Acid," by R. H. Pickard and A. Neville.

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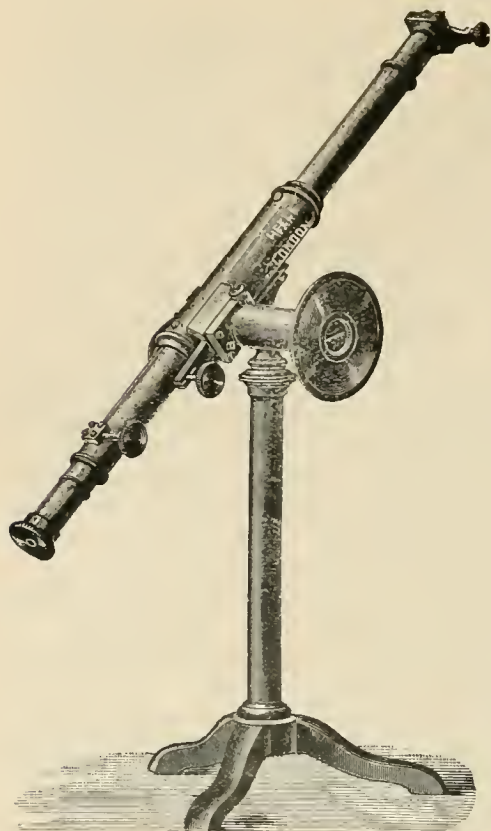
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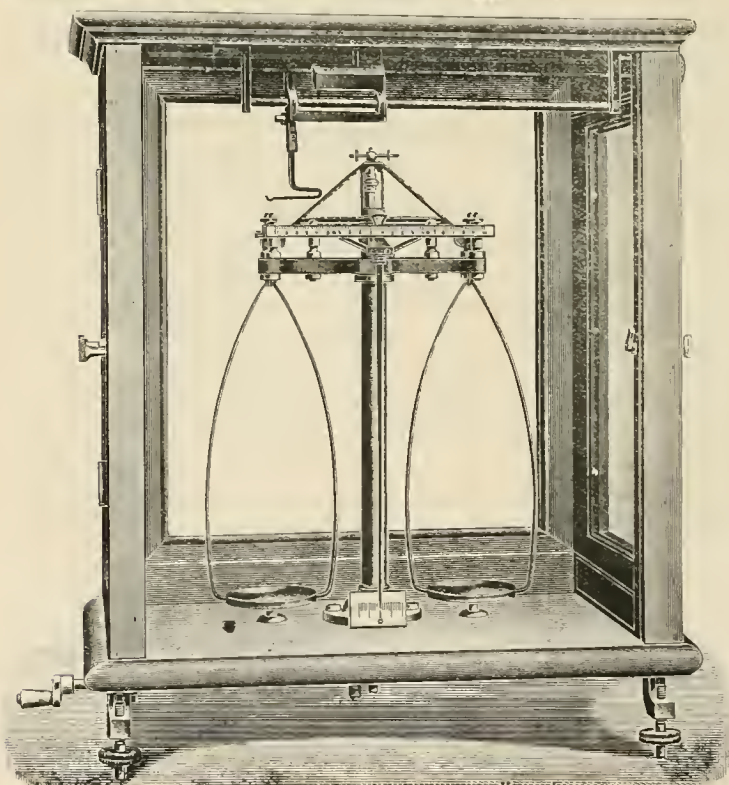
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THE CHEMICAL NEWS.

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THE THEORY OF PHOTOGRAPHIC PROCESSES.*

PART II.—ON THE CHEMICAL DYNAMICS OF DEVELOPMENT, INCLUDING THE MICROSCOPY OF THE IMAGE.

By S. E. SHEPPARD, B.Sc., and C. E. K. MEES, B.Sc.

THE investigation of development described in a previous communication was extended by the application of microscopic methods (*Proc. Roy. Soc.*, lxxiv., pp. 447 to 473). The fact that both the silver haloid and the resulting silver are distributed through the film in the form of particles of minute but measurable size, allows us in this way to detect finer qualitative differences in, and to draw independent deductions on, the processes of exposure and development. The size of the grain is important, both from the practical point of view and from the theoretical, in the one case as bearing on spectroscopical and astronomical photography, in the other on account of the great importance of the degree of surface-extension for heterogeneous systems (Ostwald, "Lehrbuch," vol. iii., "Chem. Kinetik.," Bredig, *Arch. f. Wiss. Phot.*, 1900; "Eder's Jahrbuch," 1899, p. 357).

The method has been used previously by Abney, Abegg, Kaiserling, Ebert, and others (H. Ebert, "Eder's Jahrbuch," 1894, p. 14; Kaiserling, "Phot. Mit.," 1898, i. and ii.; Abney, *Phot. Journ.*, 1898; R. Abegg, *Arch. f. Wiss. Phot.*, 1899, vol. i., p. 109), but by far the most systematic and important inquiry is that of K. Schaum and V. Bellach (*Phys. Zeit.*, 1901-02; and especially "Die Struktur der Phot. Negative," by V. Bellach—W. Knapp, Halle, 1903; this admirable monograph contains a very complete bibliography on all points).

The work subsequently described had been carried out in part before Bellach's monograph came to our notice. The investigation was then extended beyond the limits of exposure and development given by Bellach (except in region of solarisation), and arranged to compare both with his results and those of our former paper. As much of the detail is of chiefly photo-technical interest, only the chief results are given here; a fuller account will be published in the *Photographie Journal*.

Experimental.

Beck objective $\frac{1}{4}$ -inch and Reichart No. 8 $\frac{1}{10}$ -inch, both dry systems, and for some work Zeiss $\frac{1}{2}$ -inch cedar-oil immersion, kindly lent by Professor A. W. Porter, B.Sc. The micrometers were a stage-micrometer in $\frac{1}{100}$ m.m., an ocular calibrated on this, and an ocular in squares similarly calibrated.

Emulsion Tests.—As the study of ripening was deferred for further work, only the points bearing on the theory of development were considered. Preparations were made by dissolving a small piece of film in warm water and flattening under a cover-glass, then sealing with Canada balsam. The grains of a very thin layer thus obtained could be examined separately. Long exposure had no apparent effect.

The grain in fast plates varied somewhat in size, there being, e.g., in an Imperial Special Rapid, two species—(a) 0.0011 m.m. and (b) 0.0034 m.m. The latter were flattened polyhedra, of triangular section; in the slow plates the emulsion was practically homogeneous, the size of grain in Wratten ordinary being in mean 0.0017 m.m. It could not be ascertained with certainty whether the grain was crystalline or amorphous.

The Physical Nature of Silver Haloid Emulsions.—Bellach (*loc. cit.*, p. 34) found that in many cases the mean size of the grain diminished with careful drying. Thus, after several days' desiccation, a contraction from 0.67×10^{-3} m.m. to 0.57×10^{-3} m.m. was noticed in an Eder emulsion. This points to the grain itself possessing structure, and agrees with Quincke's views as to the nature of silver haloid emulsions (*Ann. d. Phys.*, [4], ii., 1000 *et seq.*). He considers that the AgBr "grains" are not pure AgBr, but contain gelatin. An emulsion in which the colloidal particles have flocked together forms a "spume." Liquid or jellified colloids consist of "spume" masses with liquid or solid spume-walls, enclosing very minute or invisible chambers. In haloid emulsions there is a stiff jelly containing a totally or partially solidified solution of AgBr in gelatin, in which a phase rich in AgBr has separated from a second phase poorer in AgBr, but richer in gelatin (Hardy, *Zeit. Phys. Chem.*, vol. xxx.). In the spume-walls and cells, spheres and crystals of haloid, much smaller than the measured grain, have separated.

The "adsorption" of gelatin to the AgBr agrees with Eder's researches on the separation of pure AgBr from emulsions by centrifugalising (Eder and Valenta, *Beitrag zur Photochemie*, &c., Sec. 3, p. 19).

Structure of Developed Negative.

By focussing on the top layer of particles, then down on to the lowest observable particles, the thickness of the reduced silver layer can be measured. This apparent thickness, recorded by the micrometer head of the fine adjustment, and multiplied by $n_1 n_2$, these being respectively the refractive indices of the gelatin and objective systems, gives the real thickness (Bellach, *loc. cit.*, p. 56).

With Wratten ordinary emulsion, exposed and developed as described, the negative layer was somewhat as described by Bellach:—

- Surface-area, particles not very numerous.
- Mean-layer, with characteristic forms.
- Lower zone of smaller particles, diminishing the lower they lie. This Bellach attributes to the penetration of developer, but we shall show later that a more potent factor is that the most exposed grains start development first. On ultimate development these grains reach the same size as the others.

For the thickness, the following facts were ascertained:—

- With constant development for a short time the depth of the image is independent of the exposure.
- With increased time of development the depth increases rapidly to a maximum for each exposure, after which it is constant.
- With long development the depth increases somewhat with the exposure, a limit naturally being fixed by the thickness of the film.

TABLE I.—N/10 Ferrous Oxalate.

Two minutes at 20° C.			Ten minutes at 20° C.		
No.	Exposure. C.M.S.	Thickness. M.m.	No.	Exposure C.M.S.	Thickness. M.m.
2.	2.04	0.0226	1.	0.101	0.0115
3.	4.66	0.0223	2.	0.204	0.0116
4.	7.75	0.0221	3.	0.466	0.0118
5.	12.9	0.0223	4.	0.775	0.0139
6.	27.9	0.0230	5.	1.290	0.0195
7.	54.5	0.0255	6.	2.790	0.0232
8.	113.0	0.0241			

TABLE II.—N/10 Ferrous Oxalate. Time of Development and Thickness. Exposure = 1.38 C.M.S.

Time. Minutes.	Density, D.	Thickness. M.m.
2.0	0.130	0.0200
6.0	0.280	0.0207
8.0	0.349	0.0206
10.0	0.542	0.0203
∞	0.586	0.0203

* A Paper read before the Royal Society, March 30, 1905.

Every measurement is the mean of ten, each focussing being repeated, and for various portions of the film.

On the Size of the Grain.

Many discordant observations as to the influence of exposure and development on the size of the grain have been published (Bellach, *loc. cit.*, p. 72). Our observations agree with Schaum and Bellach's for the early stages of development, but on prolonging the development the conclusions are modified. They may be expressed as follows:—

When γ , the degree of development, is low, the size of grain increases with the exposure.

As the time of development increases, the size of the grain does also, until at γ_{∞} it is independent of the exposure.

In addition to micrometric measurement of the diameter, the mean size was obtained by drawing the outline of the grains on squared paper by means of a reflecting system (*Ibid.*, p. 76), and then measuring the surface-extension. This method could not be applied to the smallest grains, for which the micrometric measurements are only approximate. The mean diameter of the "area" method is the mean between greatest and least, and is given to compare with the micrometric diameter. The results are the means of twenty observations and of ten for the area method.

Influence of Exposure.

TABLE III.—Developed Two Minutes in N/10 Ferrous Oxalate at 20° C.

No.	Exposure. C.M.S.	Micro-diameter. M.m.	Area. M.m. ² .	Mean diameter. M.m.
1.	1'03	0'00114	1'23 × 10 ⁻⁶	0'00101
2.	1'87	0'00112	1'45	0'00121
3.	3'10	0'00124	1'35	0'00123
4.	5'17	0'00135	1'82	0'00130
5.	11'8	0'00140	1'90	0'00152
6.	22'0	0'00162	2'10	0'00182

Mg = C. 920.

Mg = C. 1360.

For the exposure an intensity scale was used with constant time. Similar results were obtained by varying the time with intensity constant.

Influence of Development.

TABLE IV.—Exposure 1'38 C.M.S. Developed in N/10 Ferrous Oxalate at 20° C.

Time. Minutes.	Density.	Micro diameter (a). M.m.	Diameter (b). M.m.
2'0	0'150	0'00103	0'0008
6'0	0'280	0'00124	0'0010
8'0	0'349	0'00157	0'0014
16'0	0'542	0'00160	0'0016
∞	0'586	0'00167	0'0017

(a) For mean layer.

(b) For lower zone.

Size of Grain on Infinite Development.

For moderately high exposures and prolonged development measurements could not be made on the plate direct, so preparations were made and the grain measured and photographed.

TABLE V.—Developed to γ_{∞} in N/12'5 Ferrous Oxalate.

Exposure C.M.S.	Density.	Micro-diameter. M.m.	Area. M.m. ² .	Diameter. M.m.
2'04	0'277	0'00145	1'94 × 10 ⁻⁶	0'00135
4'66	0'966	0'00150	2'17	0'00165
7'75	1'496	0'00137	1'90	0'00152
12'90	2'400	0'00156	2'14	0'00171
27'90	3'400	0'00149	1'90	0'00159
54'30	4'39	0'00151	2'18	0'00165
209'0	—	0'00140	2'03	0'00156

Hence, generally, $G = \phi(\gamma, E)$, but at γ_{∞} G is independent of E , the exposure.

Effect of Bromide.

TABLE VI.

No.	Exposure. C.M.S.	Diameter A. M.m.	Diameter B. M.m.
1.	1'01	0'0009	Absent
2.	2'04	0'00094	Points
3.	4'66	0'00105	Points
4.	7'75	0'00114	0'0008
5.	12'90	—	0'00085
6.	27'9	0'0143 (a)	0'00103
7.	54'5	—	0'00123
8.	113'0	0'0165 (a)	0'00145

(a) From preparations.

These were developed 1'0 minutes in N/10 ferrous oxalate. A, no bromide; B, N/200 KBr.

This confirms Bellach's statement that bromide lowers the size of the grain. In addition, it should be noticed that the effect is greater the less the exposure. Also, it was found that the size of the grain diminished as the concentration of the bromide increased.

Bromide at Infinite Development.

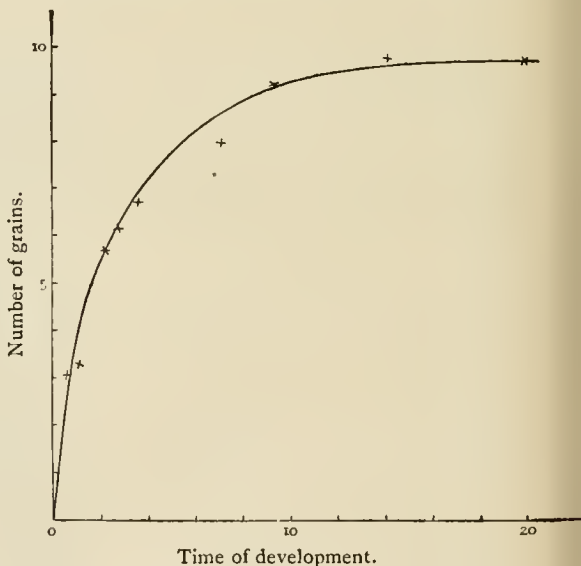
TABLE VII.—Developed to γ_{∞} in N/10 Ferrous Oxalate, N/200 KBr.

No.	Exposure. C.M.S.	Micro-diameter. M.m.	Area. M.m. ² .	Mean diameter. M.m.
1.	2'04	0'00142	1'7 × 10 ⁻⁶	0'00135
5.	27'9	0'00137	1'9	0'00142
8.	209'0	0'00172	2'0	0'00139

Mg = 920.

Mg = 1300.

On comparing this table with Table V., it will be seen that, on infinite development, the grain attains the same size in a bromided as in a non-bromided developer.



CURVE I.

On the Number of Grains and Exposure.

In the Surface Area.—For this, photo-micrographs were taken at 500 diameters, and the grains counted in a given area on the negative. The values are the mean of twenty observations.

TABLE VIII.—Developed Ten Minutes in N/10 Ferrous Oxalate.

No.	Exposure, C.M.S.	No. per visual area.	No. per 1 m.m. ² film.
2.	0.187	17.1	192 × 10 ³
3.	0.310	16.2	181
4.	0.517	18.8	211
5.	1.18	17.8	199

Hence for moderately long development, the number of grains on the surface is constant.

In the Thickness.—These were counted directly under the microscope, with a micrometer in squares. The values are for 25 to 30 squares, readings being taken in different portions of the film. The unit volume is a prism of area 1 m.m.² and height equal to thickness of film. It was found that the number of grains increased with the exposure and for moderately long development was nearly proportional to the density. As this is contrary to Bellach's results, several sets of experiments were made, with as wide a range as practicable of exposure and development, which fully bore this out. The conclusion was further tested by making sections through the film. The best results were obtained by removing the developed film from the plate and rolling it up in gum mucilage. A small portion was then frozen on an ether spray microtome and sections cut. These gave a spiral embracing several tones, and it was easily seen that the number of grains increased with the exposure, the depth of the image but slightly. The appearance agreed with Abney's description (*Phot. Journal*, 1898):—"With small exposure the grains are congregated chiefly near the surface. As the exposure increases, the film behind fills up with particles and they crowd together."

TABLE X.—Developed Six Minutes in N/10 Ferrous Oxalate.

No.	Exposure, C.M.S.	No. per 100 m.m. ² visual.	Per unit vol.
1.	0.04	2.90	27.3 × 10 ³
2.	0.081	2.46	23.4
3.	0.184	3.21	30.2
4.	0.312	6.10	57.5
5.	0.52	7.58	71.0
6.	1.12	8.34	78.5

Mg = C. 1000.

1 and 2 were below the "Schwellenwerth." Obviously the number increases with the exposure. This was confirmed for other experiments, as far as the density permitted. Above 0.3 to 0.4 measurements could not be made; but it can be seen that on extreme development (Table V.) the size of the grain is constant. Yet the density has increased from 0.277 to 4.39, or about sixteen times. Since no commensurate increase in the size of the grain has occurred, the number must have increased.

Influence of Development.

TABLE X.—Wratten Ordinary Plate Exposed for 0.25 C.M.S. Developed in N/10 Ferrous Oxalate at 20° C.

No.	Time, minutes.	No. of grains per 100 m.m. ² visual.	Per unit vol.
1.	0.5	3.35	31.5 × 10 ³
2.	1.0	3.54	33.3
3.	2.0	6.10	57.5
4.	2.5	6.45	62.5
5.	3.5	7.20	67.8
6.	7.0	8.58	80.8
7.	9.0	10.03	94.5
8.	14.0	10.50	99.0
9.	20.0	10.40	98.9

See Curve I.

The number of grains increases rapidly at first, then more gradually until a maximum is attained. This agrees with Bellach's results.

(To be continued).

THE SOLUTION STATE.

By W. P. DREAPER, F.I.C.

OBJECTIONS have been raised to the dissociation theory originally put forward by Arrhenius on the grounds that the conditions suggested by the same are of an arbitrary nature.

It is assumed that without any counteracting force coming into play, the molecules of the solute dissociate into inter-groups or ions, positively and negatively charged, which migrate freely in an inert medium.

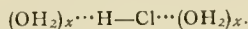
On somewhat similar lines it is perhaps possible to take exception to the modified hydrate theory recently advanced by Dr. Lowry (*Proc. Faraday Soc.*, 1905, p. 1), on the grounds that it also does not allow the possibility of any continuing action of a primary nature in this solution state.

Prof. Armstrong's suggestion that the association of the solvent molecules takes place between the solvent molecules and the negative radicals of the solute does not seem to fall in with Faraday's original proposition, when he assumed some attractive force between the opposite radicals in any two compounds.

Prof. Armstrong further suggested that the process of ionisation, as represented by this action of association, does not involve the splitting up of the molecule into separate ions.

In considering the general action of dyeing, the writer suggested a theory of solution as an alternative one, and which does not seem to entail the isolation of the hydrated ions as suggested in Dr. Lowry's later theory. It may be extended also to cover the pseudo-solution state when the modified actions are of special interest. It differs from either of the above theories or that of Brühl in assuming a constant state of equilibrium between the attractive force of the atoms in the molecule, on the one hand, and those in their total or individual effect, and the molecules of the solute on the other, or the intra-groups of the same as the case may be.

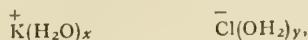
In proposing a theory to explain the general action of dyeing (*Journ. Soc. Chem. Ind.*, 1905, p. 223; and *Journ. Soc. Dyers and Colourists*, 1905, p. 136), the following example was given to illustrate the supposed action, viz.:



The association of 2x molecules of water with one molecule of hydrochloric acid is assumed to correspondingly weaken or reduce the primary bond between the H and Cl atoms, each atomic unit being under the direct influence of the solvent molecules and not the negative one only as suggested by Dr. Armstrong.

This seems to be the necessary adjunct to Faraday's law that the opposite ions will attract one another, if we assume, as I did, that the primary and secondary attractions are of the same order and interchangeable.

This action is of a different order to the one more recently suggested by Dr. Lowry (*Ibid.*), viz.,—



which assumes the hypothetical formation of ionic hydrates on lines similar to the biological process of Karyokinesis. Here we have no evidence that the primary bond is still in existence. The system is an isolated one. The two atomic units, K and Cl, are independent; the primary attraction between them is entirely replaced by that of the $(\text{OH}_2)_x$ groups as represented by their respective atomic units.

In order to explain this action, I assumed that under certain conditions the total attractive force exerted by the atomic unit A is constant, and that in the presence of the solvent molecules and by reason of their secondary or molecular attraction, the primary bond is correspondingly reduced in intensity.

This may be roughly indicated in the following way:—

If x = primary attraction and y = the secondary attraction, then—

$$A - x - A'$$

will become—

$$S_y \cdots A - (x - y) - A' \cdots S_y$$

in the presence of the solvents' molecules, S_{2y} . As y increases in intensity and the ratio of S molecule to $(A - A')$ increases, so the primary bond x will decrease in value.

In a corresponding way, and as x decreases in value, so may the chemical activity of A and A' increase. Thus solutions of mineral acids may react where the pure acid is inactive.

This solution state of the solute molecules would, from this point of view, be equivalent to a certain percentage of the units A and A' being in a free state, but actual disintegration of the molecule $(A - A')$, as assumed by Arrhenius, on the one hand or by Dr. Lowry on the other, may not be a necessary consequence of this solution state.

Under this reduced condition of primary attraction it is also assumed that atomic migration may correspondingly increase, and this would probably tend to increase the activity of the units.

From this point of view, therefore, the activity of the solute molecules will be due to the state of strain set up when x becomes $x - y$, and to the increased rate of atomic migration.

A balance between the primary and secondary attraction is set up, but y is never so great that $x - y$ becomes a negative value or is even reduced to zero; the units A and A' will always remain within the range of their respective attraction.

This action also would, except under the influence of external surface attraction, set up or tend to set up a condition of equal strain over the entire system whether the solute be in a state of solution or pseudo-solution, and not an unequal one under which the separation of some of the solute molecules into atomic groups or ions, hydrated or otherwise, is indicated.

I also assumed that the primary and secondary attraction of A are of the same order, and that the secondary attraction may be identical with molecular attraction, which at close quarters is known to be very great, and that if the molecular system is broken down it must be by some force equivalent to, or greater than, the primary bond. That such a condition of strain may explain how a "dissociation effect" may be observed in dilute solutions and an "association effect" in more concentrated ones without assuming the total suppression of the primary bond, which would render the perfectly reversible nature of solution more difficult to understand.

Also that, if this is so, the forces which we recognise as atomic and molecular are unified and brought within the range of the phenomena which we associate with gravity, it being always remembered that an intensification of Newton's law is necessary to explain the molecular effect at close quarters.

This unexplained intensity may possibly be due to the transfer of primary into secondary attraction, and may be an indication of the possible range within which this action may take place.

As suggested further on, definite sub-systems may form in the solution system, which may lead to the formation of hydrates or definite but complex aggregates. In such a case this system should be regarded as a two-phase one in the same sense that a hydrogel is considered to be one.

This hypothesis agrees with the assumed conditions of the state of pseudo-solutions put forward to explain the facts recorded in the original paper.

If we allow that (1) within certain limits of concentration, and when once an equilibrium is established, and where the action is a reversible one, the aggregates in any solution are of equal size, and (2) the aggregates in a stronger pseudo-solution are larger in direct relation to the number of molecules (of the solute) present, and when

once a certain point is reached they increase in size rather than number; and that this solution state is assumed to be the result of the equilibrium between these respective attractive forces.

Then the conditions which exist and cause the alterations in the freezing- and boiling-points of the solvent on addition of the solute may possibly be explained in this way from one end of the solution scale to the other.

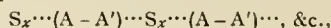
If we assume that the ionic effect is produced by the partial separation of the solvent molecules as indicated by the ionic hydrate theory, we have no explanation why the remaining solution molecules do not behave in a normal way.

The reversal of the action, too, in strong solutions will be due to the more definite grouping due to molecular hydration, in the same way that pseudo-solutions form hydrogels. It seems natural that in stronger solutions, where the solute molecules are in closer contact, that their mutual attraction will correspondingly increase, especially as at the same time the ratio of the molecules of the solution to solute decreases. This will bring about an increasing tendency for what may be called "grouping," in which the proportion of solute molecules in the complex will naturally increase.

Conductivity of Solutions.—It is generally assumed that the passage of a current is due to the presence of free ions. The passage of charged ions carrying with them innumerable associated molecules of water is a difficult one to conceive.

It may be mentioned here also that certain colour changes which have been attributed to the presence of free ions will take place where dissociation is said to be absent (Kahlenberg, *Trans. Faraday Soc.*, 1905). Is it not as reasonable to assume that association effects of a certain kind may afford free paths for the electrical distribution of energy through space?

If we consider a hypothetical system of linking as indicated—

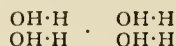


we arrive at a possible free path for energy and even possible lines of atomic migration of an abnormal character in the presence of an independent flow of electrical energy.

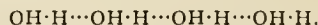
As x decreases in value the rate of flow would be facilitated by the formation of a number of extra free paths.

The colour effects produced may be due to the condition of strain $A - A'$ rather than to the ionic effect.

Dr. Lowry says "the affinity of water molecules for H and OH must be relatively slight, since otherwise liquid water would be a good conductor." Yet water is generally regarded as an associated liquid. It may be that the aggregates are grouped rather than linked up in this case.



may represent the condition rather than—



It is necessary to point out that this chain hypothesis is different to the Grothaus one. In the latter case it was assumed that the breaking down of the chain was necessary before electrolysis could take place, and that a certain electromotive force was necessary to accomplish this. Further work has shown that this is not so when the poles are of the same metal as that of the salt in solution.

The "chaining up" of the associated molecules is suggested as the cause of the conducting power of the so-called electrolytes.

When this is absent the solution is a non-conductor. Association in this case means grouping such as we presumably get in pseudo-solutions.

The superior conducting power of solutions at higher temperatures may be due to some such change in the solution state.

It has been pointed out (*Elect. Review*, 1905) that it is an essential postulate of the "hydrate" theory of Dr. Lowry

that the ions have a greater affinity for the solvent molecules than for their companion ions.

I pointed out (*Ibid.*) that, owing to the very close quarters at which the molecular attraction increases abnormally, it is not likely that the combined pull of the solvent molecules would ever altogether displace the primary bond by direct substitution. At the same time we have no direct means of measuring the relative values of S_p and x .

It has also been pointed out that Dr. Lowry's theory does not explain the motive or reason why the solvent has this greater affinity for ions than molecules.

The term electrolyte is also of an indefinite nature. In a mixture of acetic acid and water which is the electrolyte? Neither of these solutions will conduct in the pure state. The inference is that free ions are only present in mixtures. The conditions of atomic migration would seem to apply to pure solutions. This would not conform with any theory of atomic isolation as the cause of these phenomena in solutions.

Dr. Lowry is of opinion that at low concentrations the greater part of the salt must be in an "ionised" condition, and the experimental data are fully in accord with the view that combination with the solvent is characteristic of the ion even more than the molecule.

From the point of view that the action may always be referred to the atomic units themselves this would agree with the above views. However, granted that the primary and secondary attractions are identical so far as their origin is concerned, it would seem natural to assume that the primary bond will always be the stronger, and that this would prevent ionisation.

If we assume that the partial or selective action takes place, leading to the isolation of ions or molecules of the solute and their removal from the active sphere of the solution, it must be remembered that in similar conditions in pseudo-solutions, where some such grouping undoubtedly takes place, the influence of the salt on the solution and its physical constants is reduced.

Why, if 1 molecule of any substance be dissolved in 100 molecules of a liquid of a different nature the lowering of the freezing-point is nearly constant, and that if an ion corresponds with a molecule in its influence that a value of double the original factor (0.63°) will indicate dissociation into two ionic groups, or three as the case may be, and that these higher figures have been recorded in some cases, is held to indicate dissociation.

Why should not these abnormal figures equally well indicate association (in weaker solutions) to a correspondingly increased extent? In this case it would be assumed that double the number of solvent molecules would be held in association, and that in stronger solutions, where the ratio of solute to solution would be in favour of the former, this phenomenon would give place to a more simple association effect for want of sufficient molecules of the solution to go round.

The explanation offered by Jones and Chambers (*Am. Chem. Journ.*, xxiii., 103), that in the case of abnormal cases in freezing-point experiments with substances which are hygroscopic, the solute combines with large numbers of solvent molecules and removes them from the sphere of action, hardly explains why the other and remaining solvent molecules which are still in the sphere of action, do not act in the normal way. If, however, we assume in this case that the action is a general but abnormal one of attraction between the solvent and solute molecules, it is held that it is easier to assume that association is the cause of this abnormal action in so-called hygroscopic bodies than that it is due to ionic splitting, when it is remembered that in the hygroscopic action of the salts themselves on exposure to air (moist) the attacked solution will be in a very concentrated form and not in a favourable condition for ionisation, it being remembered that it is the same hygroscopic substances which give abnormal results in more dilute solutions as noticed above.

Saturation-point.—A solution will become saturated

when an equilibrium is established between unit mass of the solution and a further mass of the solute. The attraction of the solution for the solute will fall to zero at this point. In the case of pseudo-solutions when the action is complicated by the production of aggregates of the solute, either alone or in conjunction with solvent molecules, the presence of a more soluble salt will displace the solute. This is seen in the "salting out" of colloids.

Again, as Kahlenberg has pointed out, the ionic theory in its application to the precipitation of colloids breaks down. The attempts to ascribe the precipitation to the presence of free ions which the precipitating electrolyte is supposed to supply, are discounted by the fact that the power of coagulating colloids is not confined to electrolytes.

In conclusion, therefore, it is suggested that the balance between the two forces which we call molecular and atomic respectively may explain the phenomena met with in solutions of crystalloids or colloids in a more satisfactory way than assuming the formation of "hydrated ions" on the one hand, or the isolation of ions in a negative medium on the other. It is necessary, however, to assume that these two forces are really one and the same, the difference being one of degree; that the intensification of Newton's law at close quarters is due to the weakening of the primary bond and consequent increase in the effective and rapidly increasing attraction between molecule and molecule at close quarters, due to the transfer of primary into secondary attraction.

The presence of hydrates or definite solution solute aggregates is a secondary matter. The conductivity of a solution depends on the "linking up" of solution and solute molecules. The increased "activity" of the solute in solution is due to this weakening of the primary bond and possibly the consequent increase in atomic migration.

In solutions which do not conduct the "linking up" is replaced by "grouping" of a similar nature to that seen in pseudo-solutions. This is caused by the attraction of the solute molecules for one another being relatively greater than that of the solution molecules for the solute.

The presence of a larger series of hydrates is also of a more complicated nature than that of general association, which at certain points may lead to such marked grouping effects that they persist into the solid state.

Roscoe's experiments on the indifferent points in solutions confirming the idea that definite hydrates were not formed, shows that the relation between solvent and solute is a more closely balanced and reversible action than that indicated by the term hydration. Variations of such outside influences as reduction in atmospheric pressure had a marked effect on the experimental results obtained. Such a delicately adjusted equilibrium between the solvent and solute as that indicated, and which is subject to slight variations in the vapour pressure of the latter, hardly indicates the formation of definite compounds.

The production of eutectic mixtures also indicates a very loose attraction between the solvent and solute. But in both cases and under standard conditions this balance is so set up that in the one case the solute and solvent will distil together in constant ratio, and in the other they will be thrown out of the system in the solid state in a definite but independent ratio.

In conclusion, therefore, it is suggested that in the present incomplete state of our knowledge there is as much evidence in favour of the above modified association theory as there is in favour of the one which assumes the presence of "hydrated" ions.

Also that if we assume these conditions we may possibly find in them some explanation of the different phenomena exhibited in the three states of matter. In the liquid form the molecules have so far approached each other that the transfer of the primary attraction into secondary attraction is coming into play, but is not yet sufficient to prevent molecular migration.

In the solid state the transfer is more complete, and an actual linking may take place, and an internal condition of

strain set up which may account for the different conditions set up in solids as shown by our physical measurements.

Also molecular migration is slowed down or even entirely prevented, as is seen in the well known experiments on this subject.

This transfer similarly explains the abnormal attraction at short distances as exhibited in nature which is said to be greatly in excess of that required by Newton's law.

SOME OBSERVATIONS ON COLUMBIUM.*

By ROY D. HALL and EDGAR F. SMITH.

(Continued from p. 222).

ONE hundred grms. of the residues obtained by the evaporation of mother-liquors (see p. 221) to dryness were dissolved in water and fractionally crystallised. After having removed as much of the tantalum as possible by introducing dilute potassium hydroxide into the boiling solution until a rather considerable and permanent precipitate was obtained, the solution was boiled for some time. The first fraction of crystals (2) and the third fraction of crystals (3) were removed, after which hydrofluoric acid was added to the mother-liquor, from which there separated a crop of needles, which we shall designate Crystals 4. These last were re-crystallised from hydrofluoric acid. They probably contained silicon and tantalum. The acid mother-liquors from these different crops of crystals were treated as described by Hermann (*Journ. Prakt. Chem.*, 1877, [2], xv., 105); that is, they were treated with 20 parts or 2 litres of water and 150 grms. of sodium hydroxide. A clear solution resulted, from which a fine crystalline precipitate separated. The filtrate from this precipitate gave no reduction test when treated with acid and zinc, nor was anything obtained from it after having added dilute sulphuric acid and a slight excess of ammonium hydroxide. It was free from earthy bases and metallic acids.

The crystals of the sodium salt (2.5 grms.), obtained as outlined in the last paragraph, dissolved almost completely in 20 parts of boiling water, and separated in well-defined forms from the cold solution. A portion of this salt heated in a salt of phosphorus bead imparted a blue colour to the latter in the reducing flame.

The next step was to decompose the solution of this crystalline sodium salt with dilute sulphuric acid. The solution was hot. The precipitate which separated was thrown upon a filter and washed, after which it was dissolved in hydrofluoric acid and an equivalent amount of potassium carbonate added in order to form potassium-columbium oxyfluoride. The solution was evaporated to dryness upon a water-bath, the residue repeatedly moistened, and evaporation to dryness repeated until the odour of hydrofluoric acid could not be detected by the smell; then the salt was baked, taken up in water, and the solution boiled for some time. A trace of tantalum oxyfluoride separated. It was filtered out. On evaporation to crystallisation the leafy characteristic crystals of potassium-columbium oxyfluoride appeared. They were dried between bibulous paper and then analysed.

Analysis.

0.5502 grm. of salt gave 0.2452 grm. of oxide and 0.3224 grm. of potassium sulphate.

0.2452 : 0.3224 :: $x/2$: 174 $x = 264.6$.

	Calculated, $K_2CbOF_5 \cdot H_2O$.	Found.
Oxide	44.52	44.56
K_2SO_4	57.81	58.60

A portion of crystals No. 4 was re-crystallised and analysed.

Analysis of Re-crystallised portion of Crystals 4.

0.5588 grm. of sample gave 0.2407 grm. of oxide and 0.3232 grm. of potassium sulphate.

0.2407 : 0.3232 :: $x/2$: 174	$x = 259.2$.
	Calculated, K_2CbF_7 .
Oxide	43.93
K_2SO_4	57.05
	Found.
	43.08
	57.84

The results of analysis as well as the behaviour points to the fact that the oxide contained in these residues is mainly columbium oxide, Cb_2O_5 , with a small portion of another oxide causing the equivalent weights obtained to be too low. These results may in part be due to the presence of some potassium silicofluoride, but more likely to potassium-titanium fluoride. Yet these last fractions of double fluoride in which the titanium should be concentrated show only very small amounts. Starting with so much material the last fractions should show more titanium if it is present in the mineral in appreciable amounts.

The only test for small amounts of titanium which we have are the hydrogen peroxide test of Schön (Jahresberichte, 1893, 901) and the chromotropic acid test used by Geisow ("Dissertation," 1902). Of these the former is the only one relied on, and it offers the only direct evidence which we have for the presence of titanium in the potassium-columbium oxyfluoride obtained from columbite.

The methods applicable in the preparation of columbium oxide relatively free from titanium are as follows:—

1. Crystallisation of potassium-columbium fluoride, K_2CbF_7 , which is not isomorphous with potassium titanium fluoride. The difficulty in this case is that the hydrofluoric acid increases the solubility of the columbium body and decreases that of the titanium double fluoride, so that the titanium would have less tendency to concentrate in the mother-liquors.

2. Fractional precipitation with dilute ammonium hydroxide. The columbium hydrate is precipitated first and the titanium concentrated in the last fractions. No fraction consists entirely of titanium hydrate; even the last fraction is largely columbium hydrate.

3. The formation of the chloride or oxychloride of columbium and the chloride of titanium and separating these by distillation.

4. Treatment of the hydrates with cold, fairly concentrated sulphuric acid, in which the titanium hydrate should dissolve and leave the columbium.

All of these methods were tried in the endeavour to obtain sufficient titanium from the columbium to identify it and prepare some of its derivatives, e.g., the potassium double fluoride. In order to try our Method 1 the remainder of the residues—2 to 3 kilos.—was crystallised twice from hydrofluoric acid, thus getting potassium columbium fluoride, K_2CbF_7 . The mother-liquors were united. They equalled 600 c.c. They were neutralised with dilute ammonium hydroxide; the precipitated hydrate filtered out and the filtrate made alkaline with a large excess of ammonium hydroxide, which gave a further precipitate. This last hydrate was filtered out and dissolved in hydrofluoric acid. Potassium carbonate was added and the solution evaporated to dryness on a water-bath, the residue taken up in water and crystallised. The crystals obtained were short stubby needles. They were evidently not potassium-columbium oxyfluoride, K_2CbOF_5 . Their quantity was too small to re-crystallise, but they were analysed:—

0.4672 grm. of sample gave 0.1740 grm. of oxide = 37.6 per cent.

0.4672 grm. of sample gave 0.3050 grm. of K_2SO_4 = 65.3 per cent.

The specific gravity of the oxide was found to be 5.2, although too little of it was at hand for accurate work. The determination of the titanium in the oxide colorimetrically gave 0.0106 grm. of TiO_2 = 6.1 per cent.

* Proceedings of the American Philosophical Society, 1905, xliv., p. 177.

The salt originally taken showed 0.62 per cent of its oxide to be TiO_2 by the colorimetric determination, while the double fluoride of potassium and columbium obtained showed a TiO_2 content equal to 0.25 per cent of its oxide. Hence it would seem that by Method 1 the titanium or oxide with lower specific gravity and molecular weight did concentrate in the mother-liquors.

Crystals 2 and 3 (see *ante*) were combined. Their total weight was about 1 kilo. This, in portions of 100 grms. at a time, was dissolved in about 2 litres of water and fractionally precipitated with ammonium hydroxide, using dilute alkali and working in the cold with constant stirring. The alkali was added until the solution was barely acid to litmus; the precipitate formed was filtered off and the filtrate made alkaline with an excess of the precipitant. This second fraction contained about 3 to 4 grms. of oxide from each 100 grms. of double fluoride taken. These ten last fractions were combined and dissolved in hydrofluoric acid, 15 grms. of potassium hydroxide added, then dilute ammonium hydroxide until slightly acid, and the precipitate filtered out. It was marked A. Ammonium hydroxide was then added to the filtrate until litmus showed the reaction to be just neutral. The precipitate was designated B. C was obtained in the filtrate from B by adding a large excess of ammonium hydroxide. It (C) presumably should contain most of the titanium from the 1000 grms. of double fluoride taken. The oxide actually present in it was changed to double fluoride by dissolving in hydrofluoric acid and adding potassium carbonate. The first crop of crystals was obtained from strong hydrofluoric acid. It re-crystallised from the same in needles. These were analysed:—

0.6954 grm. of the sample gave 0.3018 grm. oxide and 0.3900 grm. potassium sulphate.

0.3018 : 0.3900 :: x : 174 x = 269.3.

	Calculated, K_2CBF_7 .	Found.
Oxide	57.05	56.09
K_2SO_4	43.93	43.40

The specific gravity of the oxide equalled 4.45. 0.3 grm. of it showed the presence of the equivalent of 0.0025 grm. of TiO_2 , or 0.83 per cent.

The needles from C, not taken for analysis, and the mother-liquor were combined and evaporated to dryness on a water-bath to expel the excess of hydrofluoric acid. This was repeated once. The solution of the salt was then fractionally precipitated with ammonium hydroxide, the fractions up to the point where litmus showed a slightly alkaline reaction being discarded, when the filtrate from them was made strongly alkaline with ammonium hydroxide. The precipitate obtained was changed to its potassium double fluoride. About 2.5 grms. of the double salt were got.

Analysis.

0.7248 grm. of sample gave 0.3014 grm. of oxide and 0.4205 grm. of K_2SO_4 .

0.3014 : 0.4205 :: x : 174 x = 249.4.

	Calculated, $\text{K}_2\text{C}_2\text{OF}_5\text{H}_2\text{O}$.	Found.
Oxide	57.81	58.02
K_2SO_4	44.52	41.58

The specific gravity of the oxide was found to be 4.667. 0.2930 grm. of oxide gave a colour with hydrogen peroxide equivalent to 0.0322 grm. of TiO_2 = 11 per cent.

The crucible in which the oxide was ignited was deeply stained. The analysis and the colour test showed the presence of titanium, while the stain on the crucible and the high specific gravity of the oxide could be due to tin in considerable amount, which is precipitated in the last fractions on fractional precipitation with ammonium hydroxide.

(To be continued).

Welfare Work.—The endeavours of Messrs. Burroughs, Wellcome, and Co. to promote the moral, mental, and physical betterment of their people has received recognition at the Liège International Exhibition just closed. A special Gold Medal was conferred upon them for the "Intellectual and Moral Development of Workers."

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

THE following are abstracts of papers received during the vacation, and published or passed for publication in the *Transactions*:

139. "Synthesis from Glucose of an Octamethylated Disaccharide. Methylation of Cane-sugar and of Maltose." By THOMAS PURDIE and JAMES COLQUHOUN IRVINE.

When a solution of tetramethyl glucose in pure benzene containing hydrogen chloride was heated at 105–115°, water was eliminated, and the rotatory power increased. The product, when distilled under reduced pressure, was a neutral dextrorotatory syrup without multirotation, which was devoid of action on Fehling's solution. The results of combustion and of methoxyl estimation agreed with the composition of an octamethylated disaccharide. Moreover, tetramethylglucose, which was recovered by heating the compound with dilute hydrochloric acid, appeared to be the sole product of the hydrolysis. These results indicate that condensation had occurred between two molecules of tetramethylglucose in the γ -oxide form, the product being an octamethyl glucosido-glucoside, which appears to be the first example of a synthesised disaccharide of the non-reducing type, represented by cane-sugar and trehalose.

140. "Studies in the Acridine Series. Part II. Action of Methyl Iodide on Benzoflavine." By JOHN THEODORE HEWITT and JOHN JACOB FOX.

The authors have extended their work on 2-amino-3:7-dimethylacridine (*Trans.*, 1904, lxxxv., 529) by an examination of benzoflavine (2:8-diamino-3:7-dimethyl-5-phenylacridine). Acetylation with acetic anhydride and fused sodium acetate has furnished a diacetyl and small quantities of a tetraacetyl derivative.

Diacetylbenzoflavine gives a methiodide, $\text{C}_{26}\text{H}_{26}\text{O}_2\text{N}_3\text{I}$; ammonia acts on this giving a base $\text{C}_{24}\text{H}_{25}\text{ON}_3$, one molecule of acetic acid being removed in addition to hydroiodic acid.

By complete hydrolysis (that is, a removal of both acetyl groups), salts are obtained of which the sulphate, $(\text{C}_{22}\text{H}_{21}\text{N}_3)_2\text{H}_2\text{SO}_4$, may be regarded as having a typical composition. The corresponding base does not contain oxygen, and since it lacks a carbinol hydroxyl its constitution must be regarded as para-quinonoid.

141. "Note on certain Derivatives of Cyclopropene." By DAVID TREVOR JONES.

The diethyl ester of methyleyclopropenedicarboxylic acid and the corresponding dimethyl ester both readily take up two atoms of bromine, ethyl dibromomethyltrimethylenedicarboxylate thus obtained being a liquid (b. p. 185.30° m.m.), whilst the dimethyl bromo-ester is a solid (m. p. 77°). When warmed with zinc and acetic acid, these additive products yielded the cyclopropene esters from which they were derived.

When ethyl dibromomethyltrimethylenedicarboxylate is condensed with two molecules of ethyl sodiomalonate, a non-volatile product is obtained, which, on saponification with potassium hydroxide, yields small quantities of a tribasic acid, $\text{C}_9\text{H}_5\text{O}_8$ (m. p. 222°).

The intermediate non-volatile product appears to contain ethyl methylcyclopropanetetraacetyl, the acid, $\text{C}_9\text{H}_5\text{O}_8$, owing its formation to the splitting of a linking by potassium hydroxide with subsequent lactone formation.

142. "Experiments on the Synthesis of the Terpenes. Part V. Derivatives of Ortho-cymene." By FRANCIS WILLIAM KAY and WILLIAM HENRY PERKIN, jun.

Terpenes belonging to the *o*-series have not previously been prepared, and the authors described a series of experiments by which many members of this group have been obtained.

143. "Experiments on the Synthesis of the Terpenes. Part VI. Derivatives of Meta-cymene." By WILLIAM HENRY PERKIN, jun., and GEORGE TATTERSALL.

The authors dealt with some hitherto unknown members of the *m*-series of terpenes which have been obtained from various derivatives of *m*-toluic acid with the aid of organo-magnesium compounds.

144. "Topic Axes and the Topic Parameters of the Alkali Sulphates and Selenates." By ALFRED EDWIN HOWARD TUTTON.

The conception of "topic axes," a combination of the crystallographical axes with the molecular volume, introduced independently by Muthmann in Germany and the author in this country, has proved of great great value as an expression of the fundamental morphological structure of crystals. The author's surmise, published in 1894 (*Trans.*, lxx., 659), as to the existence of relatively large interspaces between the structural units, has now been proved to be a fact by the results of the determinations of the topic axes of the ammonium salts.

The importance of correctly diagnosing the type of homogeneous structure present in a crystallised substance is emphasised, and the suggestion of Fedoroff (*Zeit. Kryst. Min.*, 1902, xxxv., 129), that the type present in the crystals of the alkali sulphates and selenates is a pseudo-hexagonal one, is taken up and shown to be probably in accordance with fact, although the symmetry is strictly rhombic; for the primary prism angle is less than 1° removed from 60° , and the crystals frequently show a pseudo-hexagonal habit and form pseudo-hexagonal triplets.

A new series of topic axes has therefore been calculated for these salts on the assumption of a pseudo-hexagonal space lattice, employing densities freshly determined with the aid of the suspension method for the calculation of the molecular volume involved. The results demonstrate even more elegantly the laws already published by the author, governing the relations of the morphological constants with the atomic weight of the alkali metal, and with that of the dominant negative element (sulphur or selenium) present, as also the rule regarding the position of ammonium near rubidium in the alkali series and the interesting corollary as to the existence of intermolecular and inter-atomic spaces.

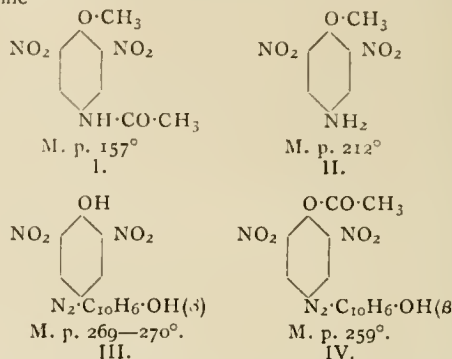
145. "The Relation of Position Isomerism to Optical Activity. IV. The Rotation of the Menthyl Esters of the Isomeric Nitrobenzoic Acids." By JULIUS BEREND COHEN and HENRY PERCY ARMES.

The previous observations on the effect of position isomerism on the rotation of menthyl benzoate have been confirmed. The *p*-nitro-group has the least, the *o*-nitro-group the greatest effect on the rotation, whilst the effect of the *m*-nitro-group lies between the two. The most striking difference in the effect of the nitro-group and that of the halogens previously studied (*Trans.*, 1903, lxxxiii., 1213; 1904, lxxviii., 1262) is that, whereas the ortho-chlorine and -bromine diminish the amount of deviation, the *o*-nitro-group enormously increases it.

146. "Dinitroanisidines and their Products of Diazotisation." By RAHAEL MELDOLA and FRANK GEORGE COAD STEPHENS.

This paper is in continuation of former work on the elimination of a nitro-group on diazotisation, and has been carried out in order to ascertain whether this elimination follows the ortho-para rule. The authors have found that when dinitro-*o*-anisidine is diazotised in presence of sulphuric acid and the product decomposed by heating with hydriodic acid, there is obtained a mixture of a new iododinitroanisole ($\text{C}_6\text{H}_2\text{OCH}_3 \cdot 1\text{NO}_2 \cdot 2\text{NO}_2 - 1:2:4:5$), melting at $146-147^\circ$, and the iodonitroresorcinol methyl ether (m. p. $115-116^\circ$) formerly described. This result shows that under the conditions of diazotisation specified there results a mixture of a diazonium salt and a quinone-diazide (diazo-oxide). By the nitration of the monoacetyl derivative of *p*-aminophenol the authors have obtained, in accordance with the results recently published by Reverdin (*Arch. Sci.*

Phys. Nat., 1905, xix., 353), the acetyl derivative of the isopiramic acid ($\text{C}_6\text{H}_3\text{OH} \cdot \text{NO}_2 \cdot \text{NH}_2 \cdot \text{NO}_2 = 1:2:4:6$) of Dabney (*Am. Chem. Journ.*, 1883, v., 33). On methylation, this acetyl derivative yields a new dinitroacetaniside which, on hydrolysis, gives a new dinitroanisidine



The latter on diazotisation does not lose a nitro-group, but the methyl of the methoxy-group is eliminated with the formation of the dinitroquinonediazide. The latter couples with β -naphthol in alkaline solution to form the azo-compound (III), the acetyl derivative of the latter (IV.) being readily formed by heating the compound for a few minutes with acetic anhydride.

The authors have also prepared the dinitroacetaniside and dinitroanisidine corresponding to the new dinitroaminophenol recently described by Reverdin.

147. "Labile Isomerism among Benzoyl Derivatives of Salicylamide." By ARTHUR WALSH TITHERLEY and WILLIAM LONGTON HICKS.

A compound erroneously described by one of the authors (*Trans.*, 1902, lxxx., 1533) as salicylbenzamide, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$, melting at 120° , which was obtained in the condensation of methylsalicylate and sodium benzamide, was shown to be a peculiar double compound of benzamide and salicylic acid, and *N*-benzoylsalicylamide has not yet been isolated. There are, however, two *o*-benzoyl derivatives of salicylamide, one melting at 208° , obtained in the above condensation, which is identical with the compound described by Gerhardt and Chiozza (*Ann. Chim. Phys.*, 1856, xli., 139), the other (m. p. 144°) obtained by the authors by the wet benzoylation of salicylamide by benzoyl chloride in presence of sodium carbonate. Neither gives any colouration with ferric chloride, and there is strong evidence that in both compounds the benzoyl group is attached to phenolic oxygen. The more fusible isomeride is labile, and passes with remarkable ease into the other, the transformation in most cases being quantitative.

The change, however, is not reversible, and of the two it is the labile compound which must possess the ordinary amide structure, $\text{BzO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH}_2$, since only the stable form, *o*-benzoylsalicyliminohydroxide, $\text{BzO} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{NH}$, yields metallic salts.

Both forms on benzoylation in pyridine yield the same *O*-*N*-dibenzoylsalicylamide, $\text{BzO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NHBz}$ (m. p. 129°), the stable substance giving a theoretical yield, the labile isomeride furnishing a much smaller proportion owing to simultaneous production of benzoylsalicylnitrile. There is evidence of the existence of two forms of the dibenzoyl derivative in equilibrium when the stable form melting at 129° is fused. On rapidly cooling, a brittle, amorphous glass is obtained which melts at $55-60^\circ$, solidifies again at 85° , and then melts at 128° .

148. "Preparation of Benzencazocoumarin; its Pearing on the Constitution of *p* Hydroxyazo-compounds." By HERBERT VICTOR MITCHELL.

The existence, and extreme ease of formation, of

benzeneazocoumarin and the three nitrobenzeneazocoumarins favours the view that the *p*-hydroxyazo-compounds are really phenolic in character and not derivatives of quinonephenylhydrazine.

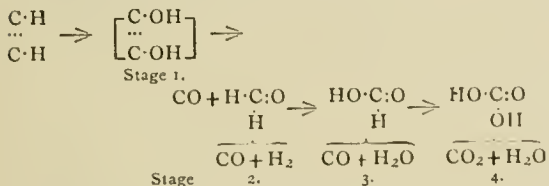
149. "The Combustion of Acetylene." By WILLIAM ARTHUR BONE and GEORGE WILLIAM ANDREW.

The authors' experiments proved that—
1. The combustion of acetylene does not involve the preferential oxidation of either carbon or hydrogen. Separation of carbon or hydrogen, when it does occur, must be entirely ascribed to secondary thermal decompositions.

2. Carbon monoxide and formaldehyde simultaneously arise at an early stage of the process, probably as the result of the decomposition of an unstable primary product

$\text{C}\cdot\text{OH}$
 $\text{C}_2\text{H}_2\text{O}_2$, such as $\dots$. The formation of formaldehyde

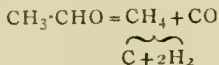
certainly precedes that of steam. The whole process may be represented by the following scheme:—



Below the ignition point, the formic and carbonic acids produced at Stages 3 and 4 respectively break down, forming steam and oxides of carbon, whilst above the ignition point the formaldehyde produced at Stage 2 (or possibly also the dihydroxyacetylene at Stage 1) is resolved into carbon monoxide and hydrogen. The explosive combustion may therefore be represented by the empirical equation $\text{C}_2\text{H}_2 + \text{O}_2 = 2\text{CO} + \text{H}_2$ (see Bone and Cain, *Trans.*, 1897, lxxi., 26).

3. Below the ignition point, excess of oxygen over and above an equimolecular proportion always retards the combustion. This was also shown to hold good above the ignition point by H. B. Dixon in his experiments on the rates of explosion of acetylene-oxygen mixtures (*Phil. Trans.*, 1893, clxxiv., 183).

4. In contact with a hot catalysing surface, such as porous porcelain, acetylene unites with steam, forming acetaldehyde. This action may take place even in presence of oxygen, and introduces a complication whenever the hydrocarbon is being burnt over a hot surface. In such circumstances, the secondary decomposition of acetaldehyde might give rise to methane, or even carbon and hydrogen and carbon monoxide, thus:—



(Bone and Smith, *Trans.*, 1905, lxxxvii., 910).

5. Benzene is not produced in presence of oxygen below the ignition point.

150. "Studies on the Origin of Colour-derivatives of Fluorene." By IDA SMEDLEY.

Experiments were made with the object of throwing further light on the question, under what conditions in ketonic compounds can halogens play the part of oxygen in contributing to the formation of coloured substances. The results supported the view that the power of the carbonyl group to act as a chromophore is destroyed by replacing the oxygen by two chlorine atoms; the effect of the other halogen atom requires further elucidation. Fluorenone chloride (m. p. 103°) was prepared and was found to be colourless, but attempts to replace the chlorine by iodine atoms were unsuccessful. Fluorenone, fluorenone chloride, and 9:9-dihydroxydiphenylfluorene (m. p. 223—224°) exhibit in a marked degree the property of "halo-

chromism" when dissolved in concentrated sulphuric acid. The action of alcoholic potassium hydrosulphide on fluorenone chloride produced a colourless disulphide (m. p. 161°); the similar action of alcoholic potassium sulphide did not form a thio-ketone, as was expected, but produced the red hydrocarbon, bisdiphenylene-ethylene and fluorenone.

151. "Note on the Zeisel Reaction in the case of Di-ortho-substituted Phenolic Ethers." By DAVID RUNCIMAN BOYD and JOHN EDMUND PITMAN.

Pyrogallol trimethyl ether is readily decomposed by aqueous hydriodic acid (sp. gr. 1.6), giving the theoretical yield of methyl iodide after heating for forty-five minutes.

Trichloroanisole and tribromoanisole, on the other hand, are left for the most part unaffected by such treatment. If, however, the solubility of these ethers is secured by employing, instead of aqueous hydriodic acid, a mixture of about equal volumes of hydriodic acid with glacial acetic acid, decomposition is complete after an hour's heating, and a theoretical yield of methyl iodide is obtained.

152. "The Mechanism of the Hydrogen Sulphide Reduction of Nitro-compounds." By JULIUS BEREND COHEN and DOUGLAS McCANDLISH.

In the process of reducing different nitro-compounds with ammonium sulphide, or, as it is usually effected, with hydrogen sulphide in an alcoholic solution containing ammonia, great differences are noticeable in the rate of reduction, in the conditions under which reduction takes place, and in the nature of the products formed. From a study of upwards of forty different nitro-compounds, the authors have laid down the following empirical rule:—The rate of reduction is increased by the presence of acidic (NO_2 , CO_2Me , Cl) groups and diminished by that of basic groups (CH_3 , NH_2), and is further affected by steric hindrance. The authors show further that the reduction occurs in at least two well-defined steps, the first being attended by the formation of a hydroxylamine compound, which is easily identified by its property of liberating iodine from potassium iodide.

153. "The Arylsulphonyl-*p*-diazoidimides." By GILBERT THOMAS MORGAN and FRANCES MARY GORE MICKLETHWAIT.

The new series of arylsulphonyl-*p*-diazoidimides (*Trans.*, 1905, lxxvii., 74 and 921) has been extended by the preparation and investigation of *toluene-p*-sulphonyl-*p*-phenylenediazoidimide, 1:3-*xylylene-4*-sulphonyl-*p*-phenylenediazoidimide, and the more complex *benzene-1:3*-disulphonylbis-*p*-phenylenediazoidimide.—



A detailed examination of the first of these compounds showed that (1) the molecular complexity of the arylsulphonyl-*p*-diazoidimides corresponds with the simplest empirical formula for these substances; (2) cold mineral acids and even glacial acetic acid bring about a disruption of the *p*-diazoidimide-complex; (3) the *p*-diazoidimides readily yield azo-derivatives when condensed in an inert solvent with the phenols and the more reactive aromatic amines; and (4) when treated with caustic alkalis, preferably in alcoholic solution, the diazonitrogen of these diazoidimides is eliminated and replaced by hydrogen.

154. "The Reversibility of Photographic Development and the Retarding Action of Soluble Bromides." By SAMUEL EDWARD SHEPPARD.

It was shown experimentally that development is a reversible chemical reaction, and for ferrous oxalate the equilibrium factors were determined quantitatively. The retarding action of bromides enabled the parts played by diffusion and chemical action to be defined, and a general theory of development on this basis was brought forward.

155. "Studies in Chlorination. III. The Progressive Chlorination of Benzene in presence of the Aluminium-Mercury Couple." By JULIUS BEREND COHEN and PERCIVAL HARTLEY.

In the present paper a description is given of the products obtained by the progressive chlorination of benzene from the monochloro- to the pentachloro-derivative. The results confirm the general rule which has been found to obtain in the case of the chlorotoluenes and the chloronitro-derivatives of benzene and toluene (*Trans.*, 1902, lxxxii., 1326, 1345; 1904, lxxxv., 1276; 1905, lxxxvii., 320), and which may be expressed as follows:—

The third substituent (chlorine atom or nitro-group) entering the dichloro- or chloronitro-benzenes or the monochlorotoluenes occupies the unsymmetrical position, forming a 1 : 2 : 4-compound; the fourth substituent (Cl or NO₂) occupies position 5.

In all the vicinal (1:2:3) chloro- or chloronitro-derivatives of benzene and toluene, the fourth substituent (Cl or NO₂) is adjacent to the other three.

There is no marked exception to this rule, which, in the majority of cases, has reference to the only product of the reaction in question; in a few cases to the main product.

156. "*The Interaction of Sulphuretted Hydrogen and Arsenic Pentoxide in the presence of Hydrochloric Acid.*" By FRANCIS LAWRY USHER and MORRIS WILLIAM TRAVERS.

It has been found that in absence of hydrochloric acid, or in presence of very small quantities of that reagent, arsenic pentoxide is rapidly reduced, so that the reaction results in the formation of the trisulphide. With increasing concentrations of the acid, up to 25 per cent strength, the product is the pentasulphide. In the case of the reaction between arsenic pentoxide and sulphur dioxide in solution, hydrochloric acid exerted a similarly marked influence in retarding the rate at which the reduction took place.

In presence of concentrated hydrochloric acid, the reaction results in the formation of the trisulphide. It was proved that in this case one has to consider the reaction of the arsenic pentoxide with the hydrochloric acid as taking place much more rapidly than that which would result in the formation of the pentasulphide. The reaction of the arsenious compound and the chlorine with the sulphuretted hydrogen is practically instantaneous.

157. "*Studies in Asymmetric Synthesis. III. The Asymmetric Synthesis of L-Lactic Acid. The Optical Activity of Fermentation Lactic Acid.*" By ALEXANDER MCKENZIE.

Samples of fermentation lactic acid from various firms were examined polarimetrically, and found to be sometimes dextrorotatory and sometimes levorotatory. The author supposed that a mixture of unequal amounts of *d*- and *l*-lactic acids is invariably produced in the production of lactic acid from sugar by bacterial agency. Active lactic acid is not so readily racemised by alkali as is active mandelic acid.

The asymmetric synthesis of *l*-lactic acid was accomplished by reducing *l*-menthyl pyruvate with aluminium amalgam, when a mixture of unequal amounts of *l*-menthyl *d*-lactate and *l*-menthyl *l*-lactate, containing an excess of the latter, is formed. When this mixture is hydrolysed by an excess of alcoholic potassium hydroxide and the *l*-menthol removed, a dextrorotatory potassium salt, containing an excess of *l*-lactate over *d*-lactate, is produced; this mixture, on acidification by a mineral acid, becomes levorotatory, and forms a dextrorotatory zinc salt.

158. "*The Action of Phenylpropionyl Chloride on Ketonic Compounds.*" By SIEGFRIED RUHEMANN and RICHARD WILLIAM MERRIMAN.

By the action of phenylpropionyl chloride on the monosodio-derivative of ketonic compounds, the acetylenic ketones are not formed, but compounds which are shown to be derivatives of dihydrofurfuran. With the acid chloride, thus mono-sodioacetylacetone yields acetylbenzylidenemethylketodihydrofurfuran (m. p. 152–153°).

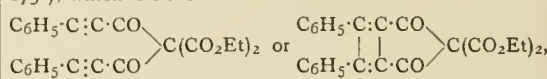
Although insoluble in alkali hydroxides or carbonates, this compound is readily decomposed by these reagents. In secondary bases, such as piperidine, it dissolves with development of heat to yield deep blue solutions, from

which hydrochloric acid precipitates an isomeric substance, 2-acetyl-5-hydroxy-4-phenyl-3-methyl-1-ketocyclopentadiene (m. p. 170°), crystallising from alcohol in red plates.

This red isomeride has acidic properties, dissolving in piperidine and alkali hydroxides or carbonates, yielding blue solutions, in which, however, it is very unstable, the colour changing to yellow, slowly in the cold but readily on warming. The solution then yields, with hydrochloric acid, the colourless acetylphenylmethylcyclobutadienecarboxylic acid, also isomeric with the former compounds. Under the influence of cold concentrated sulphuric acid, the acid is transformed into an orange compound (m. p. 216–217°), to which the name indonecyclomethylacetylene has been given. This substance dissolves in aqueous alkalis, especially on warming, yielding violet solutions.

Ethyl 5-benzylidene-2-methyl-4-ketodihydrofurfuran-3-carboxylate, the product of the action of phenylpropionyl chloride on ethyl monosodioacetoacetate, is analogous to the yellow compound, C₁₄H₁₂O₃; it also dissolves in piperidine to yield a blue solution from which hydrochloric acid precipitates a red solid similar in properties to the red compound, C₁₄H₁₂O₃.

The action of phenylpropionyl chloride on ethyl monosodiummalonate furnished a yellow compound (m. p. 174–175°), which is either—



together with the anhydride of 1:2-diphenylcyclobutadiene-3:4-dicarboxylic acid.

159. "*The Influences Regulating the Reproductive Functions of Saccharomyces cerevisiae.*" By ADRIAN JOHN BROWN.

The paper described the results of a continued investigation of phenomena associated with the reproductive functions of the yeast-cell to which attention had been previously called by the author (*Trans.*, 1892, lxi., 369; and 1894, lxx., 911).

160. "*Molecular Refractions of some Liquid Mixtures of Constant Boiling-point.*" By IDA FRANCES HOMFRAY.

Mixtures of aldehyde and water give values of specific refraction less than those calculated from the constituents, and these differences form a regular series passing through a maximum. The molecular refraction of aldehyde, CH₃·CH(OH)₂, should be less than that of acetaldehyde plus water, on account of the change of the oxygen atom from the carboxylic to the hydroxylic condition. The presence of aldehyde, together with free aldehyde and water, is therefore confirmed, and an approximate estimate of the relative amounts has been made.

Formic acid and water do not appear to combine at the ordinary temperature to form orthoformic acid. Acetone and water show a partial, but only slight, tendency to combination as CH₃·C(OH)₂·CH₃.

Gautier has given reasons for considering that a definite chemical compound is formed, consisting of one molecule of ethyl cyanide and three of alcohol, and that this is the distillate obtained in preparing ethyl cyanide by Pelouze's method.

The refractive indices of a number of mixtures of different concentrations have now been measured, and the experimental curve so constructed used to determine the composition of the distillates under atmospheric pressure and under a series of lower pressures. In the former case, Gautier's result is confirmed, but when the pressure reduced, the distillate contains more cyanide. The density and specific and molecular refractions of the mixture agree with those calculated from the constituents.

The conclusion is, therefore, that no compound is formed, and that this is a case of mutually soluble liquids of maximum vapour pressure. Cryoscopic determinations in benzene gave normal depression in the case of ethyl cyanide, but small values for alcohol and for the mixture of constant

boiling-point. Reasons are, however, given for attributing this in both cases, to reduction of osmotic pressure rather than to molecular association or combination.

CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli, No. 17, October 23, 1905.

Specific Heat of Copper Sulphate Solutions.—P. Vaillant.—The method employed by the author for the measurement of the specific heat of copper solutions is that of Joule, in which the metallic spiral which carries the current, and so heats the calorimeter, is replaced by the filament of an incandescent lamp. The substitution of the lamp for the spiral renders the method applicable to liquid conductors. As a result of a long series of experiments, the author finds that the specific heat of the dissolved sulphate rapidly increases with the concentration, and then seems to pass through a maximum. The variations can be explained by a triple influence:—1. The increase of molecular volume of the dissolved body with the dilution, which has the effect of diminishing the specific heat. 2. Electrolytic dissociation, which liberates the water of crystallisation, and has an effect similar to the above. 3. The transformation of the degree of hydration, $5\text{H}_2\text{O}$, to a state of inferior hydration which tends to diminish the specific heat at high concentrations. The specific heat of the molecule $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, calculated by Kopp's law, is 0.2832.

Composition of the Hydrochloroferric Colloid.—G. Malfitano.—Using a 5 per cent solution of sublimed iron perchloride, which is heated to 100° or 115° for fifteen to thirty minutes, a colloid is obtained of which the composition has been represented by the formula $\text{H}_n(\text{Fe}_2\text{O}_6\text{H}_6)\text{Cl}$. On filtering through collodion the greater portion of this substance is retained; this latter substance the author designates as hydrochloroferric colloid. He investigates the composition of this material.

Certain Aromatic Oxides of Ethylene.—MM. Fournneau and Tiffeneau.—In a former paper the authors described a number of ethylene oxides, and noticed their greater or less aptitude for isomerisation into aldehydes or ketones under the influence of acids or heat. They now extend their researches to three series of aromatic ethylene oxides:—The mono-substituted oxides, $\text{Ar}-\text{CH}_2-\text{CH}-\text{CH}_2$; the di-substituted symmetric oxides, $\text{Ar}-\text{CH}-\text{CH}-\text{CH}_3$; and the di-substituted asymmetric oxides, $\text{Ar}(\text{CH}_3)-\text{C}-\text{CH}_2$. They find that the former of these series of oxides are only partially isomerised under the influence of heat into the aldehydes $\text{C}_6\text{H}_5-\text{CH}_2-\text{CHO}$ and $\text{Ar}-\text{CH}_2-\text{CH}_2-\text{CHO}$. The second and third of these series, on the contrary, easily isomerise the former into arylaketenes and the latter into the aldehydes $\text{Ar}-\text{CH}(\text{CH}_3)-\text{CHO}$. None of these isomerisms are accompanied by molecular migration.

MEETINGS FOR THE WEEK.

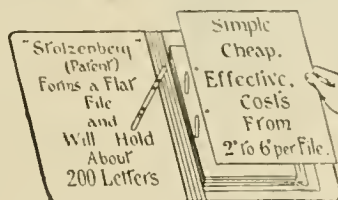
WEDNESDAY, 22nd.—Society of Arts, 8. "The Cinematograph and its Applications," by F. Martin-Ducan.

FRIDAY, 24th.—Physical, 5. "The Dielectric Strength of Air," by A. Russell. "Electrical Conductivity of Flames containing Salt Vapours for Rapidly Alternating Current," by H. A. Wilsoo. "Lateral Vibration of Loaded and Unloaded Bars," by J. Morrow.

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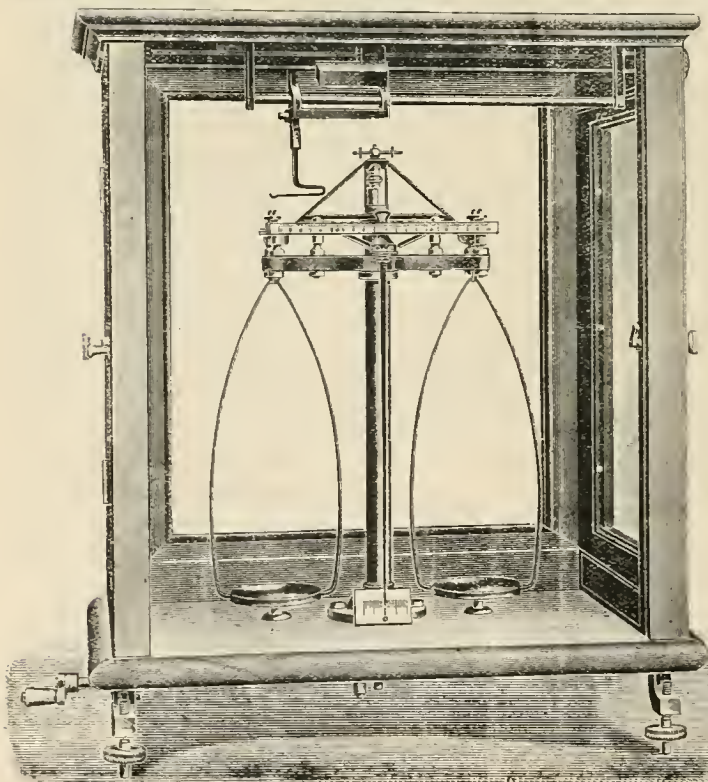
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THE CHEMICAL NEWS.

VOL. XCII., No. 2400.

THE THEORY OF PHOTOGRAPHIC PROCESSES.*

PART II.—ON THE CHEMICAL DYNAMICS OF DEVELOPMENT, INCLUDING THE MICROSCOPY OF THE IMAGE.

By S. E. SHEPPARD, B.Sc., and C. E. K. MEES, B.Sc.

(Concluded from p. 229).

Exposure through the Glass-side.

Two plates were given identical exposures behind the sector-wheel, and developed for ten minutes in N/10 ferrous oxalate at 15°. One was exposed through the glass-side; the other from film-side, but with a glass plate in front. On fixing, &c., although both showed five tones the densities of the glass-side plate were considerably less than that of the other. This agrees with Abegg (R. Abegg u. Cl. Immerwahr, *Sitz. ber. d. Wien. Akad.*, 1900, cxiv., abt. 2A) and Bellach (*loc. cit.*, p. 61).

Thickness of Negative Layer.

No.	Exposure.	Thickness (a).		D _a .	Thickness (b).		D _b .
		C.M.S.	M.m.		M.m.		
1.	10		0.0204	—	0.0192		—
2.	5		0.0199	0.110	0.0180		0.257
3.	2.5		0.0188	0.042	0.0153		0.098
4.	1.25		0.0181	—	0.0152		0.027
5.	0.62		0.0148	—	0.0152		—

(a) Glass-side.

(b) Air-side.

The depth is much the same for both plates. According to Abegg, all the grains in back-exposed plate appeared equally developed, whereas Bellach describes his preparations as similar to front-exposed plates, *i.e.*, uppermost zone with few and small particles, mean characteristic layer, and lowest with very small particles. In our plates the appearance agreed with Abegg's description, the increase in size of grain being in the opposite sense to that of a film-side exposed plate. The apparent divergence in description is probably due to the fact that Bellach used short development, one hundred and ten seconds, with a strong developer, while Abegg used prolonged stand development, more comparable with the author's conditions. The result shows that, other things being equal, the grain receiving most exposure is most reactive and starts development first.

Thus, for 1.25 C.M.S. exposure,—

		Micro-diameter.		Focus.
		M.m.	Divs.	
Film-side plate ..	{	0.00135	76.0	74.6
		0.0008		
Glass-side plate..	{	0.00106	79.5	77.0
		0.00140		

The number of grains was greater in the plate exposed from air-side. For 1 m.m.² of film,—

Air-side	132 × 10 ³
Glass-side	71 × 10 ³

while Abegg and Immerwahr give 41.0 × 10³ and

32.5 × 10³. Both the densities and the number of grains are greater for the air-side plate. Abegg attributes this to the prevention of halogen diffusion. Braun's observation on the part played by oxygen in the formation of latent images may also account for it, however (*Zeit. f. Wiss. Phot.*, vol. ii., Heft 8). Possibly connected with this is the statement of Th. Wulf that, for the so-called photo-electric effect, the sensitiveness to light increases as the potential fall of electrode to surrounding gas increases (*Ann der Phys.*, [4], ix., 946).

The general results of the microscopic survey are in agreement with the theory of development proposed before. Each grain develops as a more or less isolated system, only uniting to form "aggregates" with other grains at high exposures when the packing is closer. The thickness of the reaction-layer is from 0.02 to 0.04 m.m.—a value similar to that found by Brunner for many heterogeneous reactions. But in this case the solid phase lies entirely in the layer. The diffusion of the developer may be divided into two parts:—(a) Through the total thickness, δ ; (b) through the micro-layer, δ' , of the order 0.0005 m.m. surrounding the grain. This is the true reaction-layer, and the reaction is somewhat like to the catalysis of H₂O₂ by colloidal metals, save that there is no convection. As the diffusion has to take place through gelatine, the structure and state of this may influence the velocity. This will be dealt with later. The fact that the size of the grain with low time of development—or, better, low development-factor—varies with the exposure, indicates that the "reactivity" of the individual haloid grain is a steady function of the exposure. Hence at low development-factors departures from the law of constant density-ratios are possible, but difficult to confirm. Such departures will be the more marked whenever the chemical velocity approaches that of the diffusion process.

The conclusions given here were confirmed for other developers, and we hope to publish them later in connection with the general survey of these; since this work was finished, Messrs. Lumière (*Zeit. f. Wiss. Phot.*, ii., 256) and Wallace (*Astrophysical Journal*, 1905) have published short studies on the size of the grain. Their results do not contradict ours, but they do not seem to have considered sufficiently the effect of the degree of development, γ , on all observations.

The Early Stages of Development.—Considerable information concerning the velocity of development can be obtained from the "time of appearance" of the image, which is a function of it. In 1893 Mr. Watkins announced that for any given reducer the time of appearance gave an accurate indication of the speed of working, and that any variation in the alkali, temperature, or strength affected the time necessary to reach a given density or development-factor in the same proportion that it affected the time of appearance. Generally stated, $T_D = W T_A$; where T_D is time for density (D), T_A is time of appearance, and W is a constant.

This rule has been usefully applied in practice for timing development, but the above statement is too wide, both experiment and theory showing that such a simple relation does not hold for many complex developing solutions. The following considerations from the theory of the order of reactions explain both the rule and the deviations from it (Ostwald, "Lehrbuch," 2te Auflage, vol. ii., p. 236):—

If two analogous reactions continue to equal fractions of the total change, then the times necessary for this are inversely as the velocity factors.

Of course, it is assumed that the same function of the variables still represents the course of the reaction. If experiments with different concentrations are carried to the same fraction of these, the following relations hold:—For reactions of the first order the factors are directly, the times inversely as the concentrations, of the second order as the squares, and so on. We may apply this to development as follows:—The density which is first visible, *i.e.*, first distinction between exposed and unexposed, is a physiological constant and a fixed density, θ , say

* A Paper read before the Royal Society, March 30, 1905.

(Schwellenwerth).^{*} Hence for same exposure, *i.e.*, same final density, θ is always an equal fraction of the total density; so θ , the time of appearance, *i.e.*, for density, θ , is inversely as the velocity coefficient, and is similarly modified by concentration, &c.

With different final densities and constant developer, the values of θ are inversely as the final densities, D_1 , D_2 , &c. Here, of course, θ measures an equal fraction of the total oxidation of reducer.

Let D_1 and D_2 be any two final densities, and λ a fixed density, where D_1 , D_2 = or $> \lambda$, and let θ_1 and θ_2 be their respective times of appearance, and t_1 , t_2 corresponding times to reach λ . Then we have—

$$t_1 \theta_1 = t_2 \theta_2 = t_n \theta_n = \text{constant } W,$$

whose numerical measure is proportional to the Watkins multiple, and is independent of concentration and only dependent on velocity function.

The general theorem is only true for simple reactions, and does not hold for "graded," "catalysed," and so forth. The same limitations hold for development, and the occurrence of initial disturbances, varying in the specific developers, probably account for the wide variation of the Watkins multiple for various developers, and also its variation with the same reducer. Only for developers in which the balance between reduction-potential and diffusivity is within certain limits will W be constant, since deviations will easily occur for such a small fraction of the total change, and yet the development-function remain much the same.

The writers have extensively developed the use of the "time of appearance" for investigation of development kinetics. The most similar use of such a method of inquiry in chemical dynamics is A. von Oettingen's research on the decomposition of thiosulphate by acids, in which the "time of appearance" of the sulphur cloud was observed (*Zeit. f. Phys. Chem.*, vol. xxx.; *cf.* also H. Landolt, *Ber.*, 1886, vol. xix., p. 1317). The limiting conditions for experimental accuracy discussed there hold also for development. The time must not be so short that the limiting error of measurement seriously affects the result, nor so long as to cause doubt as to the exact moment. The observations are made in a dark room, but using as much of a steady reddish light as possible, since subsequent fogging is in general immaterial.

The timing was done with a stop-watch marking one-fifth of a second; several observations of each time were made, and the mean used, and all measurements for comparison made at one period. The method is accurate within the limits employed to about 2 per cent.

Effect of Concentration with Ferrous Oxalate.

TABLE XI.—Plate, Wratten Ordinary, Exposed 8 C.M.M.

Concentration.	T_A in secs.	Mean T_A .	$C = \text{Product}$.
0.2 N.	22.0, 19.0, 19.0, 18.8	19.7	3.94
0.1 N.	40.4, 40.0, 40.2	40.1	4.01
0.05 N.	81.0, 79.8, 80.5	80.4	4.02
0.025 N.	160.2, 158.2, 157.0	158.4	3.96
	Mean	3.98	

This shows from N/5 to N/40 the velocity is directly proportional to the concentration, even at this early stage of development.

Temperature and Development Velocity.

Experiment showed that the variation of temperature did not influence the density ratios. The effect of temperature on the velocity constant, $K = \frac{1}{t} \log \frac{\gamma_\infty}{\gamma_\infty - \gamma}$, was measured,

^{*} This fact rests on the existence of a Schwellenwerth or "threshold" value of perception of contrast by the eye.

and also on $V = 1/T_A$. In this case four series of measurements were made, embracing the range 0° C. to 30° C. By interpolation the reduced results gave the following table:—

TABLE XII.—Developed in N/12.5 Ferrous Oxalate.

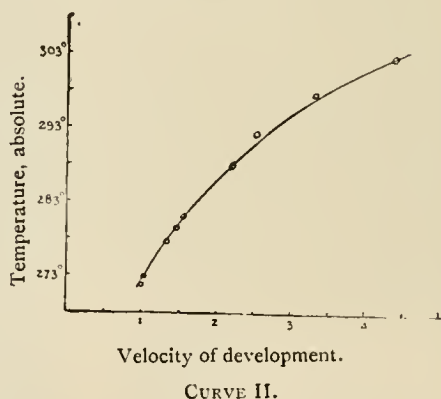
Temperature.	Absolute.	Velocity.	V. mean.
-0.8° C.	272.2	1.00	1.00
0.0	273.0	1.01	1.01
5.2	278.2	1.29	1.29
6.7	279.7	1.33	1.33
9.2	281.2	1.42, 1.56, 1.51	1.50
15.0	288.0	2.126	2.13
20.0	293.0	2.50	2.50
25.0	298.0	3.29	3.29
30.0	303.0	4.35	4.35

Van't Hoff's equation, $\frac{d \log K}{dT} = \frac{A}{T^2}$ (*Kgl. Svenska Vet. Hdl.*, 1885, vol. xxi., No. 17), in the integrated form for A sensibly constant, $\log K = -\frac{A}{T} + C$ was found to represent the results very fairly.

TABLE XIII.— C found as 7.60.

Temperature.	A.	V. obs.	V. calc.	Δ per cent.
272.0	1794	1.00	0.982	-1.8
273.0	1798	1.01	0.991	-1.9
278.2	1807	1.29	1.290	0.0
279.7	1911	1.33	1.380	+4.0
281.2	1806	1.50	1.506	+0.4
288.0	1806	2.13	2.133	+0.1
293.0	1817	2.50	2.69	+8.0
298.0	1813	3.29	3.467	+5.0
303.0	1807	4.35	4.361	+0.25

Curve calculated from $\log K = -1806/T + 7.60$.



The temperature coefficient for 10° from 0° to 30° C. is $(K + 10^\circ)/K = 1.7$.

The validity of these results is shown by measurements of K , the mean velocity coefficient.

TABLE XIV.

Temperature.	K found.	K calc.	Δ per cent
9.6° C.	0.0632	0.0632	—
20.8	0.0870	0.0891	+2.2
30.7	0.1174	0.1210	+2.0

The Temperature Coefficient.

Bodenstein (*Zeit. Phys. Chem.*, 1904, vol. xlix., p. 42) and Senter (*Proc. Roy. Soc.*, vol. lxxiv., 214) have indicated the value of the temperature coefficient for 10° as a criterion in heterogeneous reactions. For chemical reactions in homogeneous solution the value is generally about 2 to 3 (van't Hoff, "Vorlesungen," vol. i., p. 225), while Brunner found 1.5 for rate of solution of benzoic acid in water; for diffusion processes we should expect a value about 1.5, and not varying for different bodies very much.

Now we have found that the expression—

$$K = \frac{1}{t} \log \frac{\gamma_\infty}{\gamma_\infty - \gamma}$$

can be used to measure the development velocity for most developers. A preliminary study of the temperature coefficient for different emulsions and developers gave the following results:—

TABLE XV.

Reducer.	Emulsion A.	B.	C.
Fe(C ₂ O ₄)	1'60	1'90	1'70
FeF	1'52	—	—
Fe citrate	1'54	—	—
C ₆ H ₄ (OH) ₂ p. ..	—	2'10	—
C ₆ H ₄ (OH) ₂ o. ..	—	2'80	—

The temperature coefficient frequently passes the value to be expected from the diffusion theory. But in the case of development, we must be cautious in applying the criterion, as the following consideration will show:—

Beside the increase in diffusivity (mobility of reducing molecule), we must also consider—(a) Alteration of resistance to diffusion in gelatin; (b) in complex developing solutions, alteration of concentration of reducing ion by changing the chemical equilibrium, especially in alkaline developers. Under these conditions a high temperature coefficient in development does not necessarily mean that the velocity is that of a chemical reaction.

In the case of ferrous oxalate, the theoretical formula of van't Hoff, which is a deduction from the reaction isochore, was employed. This is not legitimate in the case of diffusion phenomena, and the best formulation would probably be the ordinary parabolic interpolation formula in the form $K_t = K_0(1 + at + bt^2)$; a comparison of the constants a and b for different plates and developers should yield useful information on temperature influences.

Resistance of the Gelatin.

Hardening agents, which raise the melting-point of the gelatin, are generally supposed to alter the velocity of development by changing the diffusivity. Many emulsions, however, show no such effect. Thus, with formalin (40 per cent formaldehyde) in 4 per cent strength and increasing time of immersion, although the film became quite insoluble in boiling water, the development velocity was not lowered.

TABLE XVI.

No.	Time of immersion. Secs.	T _a in secs.	Mean. Secs.
1.	0	24'0, 23'2, 24'0	23'7
2.	30	24'0, 24'2, 23'8	24'0
3.	60	24'0, 24'2, 23'4	23'9
4.	120	23'6, 24'6, 24'0	24'0
5.	240	24'0, 23'0, 23'4	23'4
6.	8 per cent, 10 mins.	25'2, 23'4	24'3

$$T = 23'9$$

The general theory of the action of hardening agents will be discussed later in connection with the destruction of the "latent image."

"Penetration" of Developer.

By the rate of penetration the time for the reducer to pass through the reaction-layer, δ , is understood. This was studied as follows:—

If plates are exposed through the glass-side, the image will lie nearer the glass, and we may expect it to appear—
a. On front first if the penetration of the developer count most.

b. On back first if the greater reactivity of the more exposed particles be the predominant factor.

A strip of Ilford ordinary film was exposed, cut up, and developed in N/10 ferrous oxalate at 15° C.

The values of T_a given are means of four experiments.

TABLE XVII.

Exposure.	T _a film-side.	T _a glass-side.
Ilford film—300 C.M.S.	40'3 secs.	45'3 secs.
60	54'6 "	52'6 "
10	72'4 "	63'0 "
Wratten ordinary—300 C.M.S. ..	94'2 "	90'4 "

Consequently, with low exposures, the back appears before the front, but as the exposure increases, the developer being the same, the two times become equal, and eventually the image appears on front first. This was confirmed on plates exposed in the sensitometer.

Plates given the same exposure from the front always show the image from the front first, the relative difference in time being somewhat greater, the absolute value of T_a always less.

The above phenomena may be explained by the following considerations drawn from the microscopy of the image:—

a. The absolute thickness of the layer of developable particles increases but slightly with the exposure.

b. Reckoning down through the layer from the exposed side, the reactivity of each layer of grains diminishes through the thickness. The slope of this reactivity-gradient then depends upon the exposure.

c. With short time of development the penetration increases rapidly; further, as the developer reaches the lowest layers, its concentration will be diminished somewhat by diffusion and oxidation by developable AgBr. There will therefore be a concentration gradient through the film.

d. Then in the case of exposure from air-side, the two gradients will be in the same direction, and will reinforce each other; for exposure from the back, the gradients will be opposite in sense, and the front layers or back will appear first according as one factor or the other predominates.

This result is in agreement with the microscopic deduction, that, other things being equal, the more exposed grains possess the greater reactivity and start developing first.

With regard to the absolute time required for the developer to penetrate the thickness of the film, an estimate can be obtained as follows:—With an Ilford film, the γ/t curve of which was known, the least time of appearance at the back for any exposure through the back was about ten seconds with N/10 ferrous oxalate at 15° C. Now, under these conditions, the half-period of development, i.e., for $\gamma_\infty = 2$, was 5.0 minutes. Hence the error due to incomplete penetration is not of a very large order, and, moreover, reasons will be given later for assuming a chemical-induction generally greater than any diffusion-induction. However, for accurate comparison of velocities, in order to avoid an erroneous time-zero, the form—

$$K = \frac{1}{t_2 - t_1} \log \frac{\gamma_\infty - \gamma_1}{\gamma_\infty - \gamma_2}$$

is the most suitable (Senter, *loc. cit.*, p. 203; see also Ostwald-Luther, "Physico-chem. Messungen," p. 455).

In development the temperature-coefficient has been found an inadequate criterion for distinguishing diffusion

from chemical velocity. Such a criterion, however, we believe to exist in the action of soluble bromides, and in a discussion of this and the reversibility of development we hope to show that the development process probably takes place in general in two phases, in the first period the chemical velocity being slow compared with diffusion, in the second the contrary holding. It is the velocity of the second period which is usually measured.

In conclusion, we have much pleasure in expressing our great thanks to Sir William Ramsay, F.R.S., for his interest in the investigation.

SOME OBSERVATIONS ON COLUMBIUM.*

By ROY D. HALL and EDGAR F. SMITH.

(Continued from p. 233).

THE crystals and the mother-liquor remaining from this salt were dissolved in boiling water and an excess of sodium hydrate added, when a heavy flocculent precipitate separated. This was filtered, boiled with water, and the insoluble portion changed to double fluoride. It was again taken up in boiling water, and an excess of sodium hydroxide added. The precipitation was not complete. The portion precipitated was treated with boiling water, filtered, and the filtrate found to contain a large amount of titanium. That portion of the precipitate insoluble in water was changed to double fluoride.

Analysis.

0.5570 grm. of sample gave 0.2248 grm. of oxide and 0.3468 grm. of K_2SO_4 .

0.2248 : 0.3468 :: $x/2$: 174 $x = 225.6$.

The sp. gr. of the oxide was found to be 4.2. The oxide gave a colour with hydrogen peroxide showing the presence of about 21 per cent TiO_2 .

Crystals "A" were changed to double fluoride and re-crystallised.

Analysis.

0.7184 grm. of sample gave 0.3188 grm. of oxide and 0.4176 grm. of potassium sulphate.

0.3188 : 0.4176 :: $x/2$: 174 $x = 265.7$.

	Calculated, $K_2C_2O_7 \cdot 5H_2O$.	Found.
Oxide	44.52	44.38
K_2SO_4	57.81	58.13

The sp. gr. of the oxide was found to be 4.481. 0.3160 grm. of oxide gave a colour with hydrogen peroxide equivalent to 0.0022 grm. $TiO_2 = 0.7$ per cent.

Crystals "B" analysed as follows:—

0.8098 grm. of sample gave 0.3614 grm. of oxide and 0.4708 grm. of K_2SO_4 .

0.3614 : 0.4708 :: $x/2$: 174 $x = 267.0$.

	Calculated, $K_2C_2O_7 \cdot 5H_2O$.	Found.
Oxide	44.52	44.63
K_2SO_4	57.81	58.14

The sp. gr. of the oxide was found to be 4.864. 0.3600 grm. of oxide gave with hydrogen peroxide a colour equivalent to 0.0013 grm. of $TiO_2 = 0.36$ per cent.

Having failed to get any evidence of the existence of neptunium in the last fractions of the double fluoride from the South Dakota mineral, it was decided to test some of the mineral from Haddam, Conn., the source of the material used by Hermann in his investigation. The last fractions of the potassium double fluoride from 5.87 kilos. of columbite from Haddam, Conn., amounting to 100 grms., were dissolved in boiling water, and an excess of sodium hydroxide added. The precipitate obtained was partly crystalline

and partly flocculent, as described by Hermann. It was filtered out, dried on a porous plate, and boiled with 25 parts of water. The crystals dissolved, leaving a yellowish residue evidently containing much iron. This residue gave a yellow coloured bead in the reducing flame containing so much iron that it was impossible with a small blowpipe to keep it all reduced. Is it not probable that this is what Hermann supposed was neptunium?

This salt was fused with acid potassium sulphate to remove the iron, the oxide remaining after extracting the fusion with boiling water was changed to double fluoride, dissolved in boiling water, and an excess of sodium hydroxide added. The precipitate obtained was crystalline and perfectly soluble in water, leaving an inappreciable residue. From all of which it may be inferred that the material from the Haddam locality showed no more evidence of neptunium than did that from South Dakota.

Ten kilograms. of the main bulk of the potassium columbium oxyfluoride were crystallised from strong hydrofluoric acid. Five hundred grms. were taken at one time, and the mother-liquors from the two fractions combined, evaporated one-half, and another crop of crystals removed. The mother-liquors from these were united and evaporated, the crystals obtained were re-crystallised, the mother-liquors from the re-crystallisation combined and evaporated to dryness with sulphuric acid. The oxide obtained from that portion evaporated to dryness was 5 grms. The fraction of crystals immediately preceding, 60 grms. in weight, was decomposed with sulphuric acid and the oxide obtained from it. The 5 grms. of oxide and about one-half of the oxide from the 60 grms. of double fluoride were heated in carbon tetrachloride vapours, taking about 2 grms. of oxide at a time. The more volatile portion, which should contain the most of the $TiCl_4$, was distilled away from the $CbOCl_3$. The portions of this liquid were combined, the oxides—3 grms.—obtained from it, and these oxides again heated in CCl_4 . Again, only the liquid portion and that of the solid which was carried over mechanically was taken. The oxide from this portion was changed to double fluoride.

Analysis.

0.5678 grm. of sample contained 0.2196 grm. of oxide and 0.3390 grm. of K_2SO_4 .

0.2196 : 0.3390 :: $x/2$: 174 $x = 225.4$.

	Calculated, $K_2C_2O_7 \cdot 5H_2O$.	Found.
Oxide	44.52	38.6
K_2SO_4	57.81	59.7

Amount of TiO_2 in the oxide 0.0594 grm. = 29.7 per cent.

The oxide from the salt taken for analysis was combined with the oxide from the double fluoride not taken for analysis, and this with the remaining half of the oxide from the 60 grms. of double fluoride mentioned above was mixed with the oxide from all the previous double fluorides which had been tested for titanium and shown its presence in a fair degree. This mixture of oxides was heated in a current of sulphur monochloride, the chloride formed collected in a receiver, and this was then heated until all of the sulphur monochloride was distilled out. This sulphur monochloride and any other chlorides which it might contain was again distilled to remove the last of the columbium chloride which might have been carried over mechanically. It was then treated with water and oxalic acid, the sulphur filtered off, and any oxide dissolved in the oxalic acid precipitated with ammonium hydroxide. This hydrate was changed to potassium double fluoride.

Analysis.

0.5444 grm. of sample gave 0.1952 grm. of oxide and 0.3850 grm. of potassium sulphate.

0.1952 : 0.3850 :: $x/2$: 174 $x = 175.9$.

	Calculated, $K_2C_2O_7 \cdot 5H_2O$.	Calculated.	Found.
Oxide	44.52	33.33	35.85
K_2SO_4	57.81	72.50	70.72

* Proceeding of the American Philosophical Society, 1905, xlv., p. 177.

0.0310 grm. of the oxide was found to contain 0.244 grm. TiO_2 , or 78.7 per cent.

A solution of the oxide in hydrochloric acid reduced with zinc to an amethyst or violet colour; the oxide also gave a violet titanium bead in the reducing flame with salt of phosphorus.

It would seem that about 80 per cent of the oxide from this double fluoride was TiO_2 .

The remainder of the double fluoride, about 0.5 grm., was dissolved in the mother-liquor from which it came by heating, and an excess of sodium hydrate added. A flocculent precipitate formed. After cooling, this was filtered off, and the filtrate acidified with hydrochloric acid, and tested for metallic acids with ammonium hydroxide. A precipitate was obtained, which was filtered out, and, after washing thoroughly, dissolved in hydrochloric acid.

Upon passing hydrogen sulphide through this solution a heavy precipitate of yellow stannic sulphide was obtained, showing that tin had been carried over with the titanium by the sulphur monochloride.

The precipitate formed by the excess of sodium hydroxide was drained thoroughly and boiled up with water. Nothing went into solution as would have happened had there been any sodium columbate in the precipitate. This well washed precipitate was dissolved in hydrofluoric acid and potassium carbonate added to change it to the potassium double fluoride.

Analysis of the Crystals obtained.

0.1893 grm. of sample gave 0.0642 grm. of TiO_2 and 0.1366 grm. of K_2SO_4 .

	Calculated.	Found.
Oxide	33.33	33.91
K_2SO_4	72.50	72.16

The determination of the TiO_2 colorimetrically gave 0.0636 grm. The salt was undoubtedly potassium-titanium fluoride, proving conclusively the presence of titanium in columbite.

(To be continued).

PROCEEDINGS OF SOCIETIES.

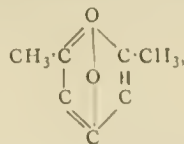
CHEMICAL SOCIETY.

THE following complete the abstracts of papers received during the vacation, and published or passed for publication in the *Transactions* :—

161. "Molecular Refractions of Dimethylpyrone and its Allies, and the Quadrivalency of Oxygen." By IDA FRANCES HOMFRAY.

In most cases of associated compounds containing oxygen, the quadrivalency of that element is probable, and the observed molecular refractions are always in excess of those derived from the additive constants. The inference is that the atomic refraction of quadrivalent oxygen is greater than the highest of the values for the bivalent atom. No satisfactory data have been published for the determination of this constant, and the compounds which appear to afford the best opportunity for such investigation are dimethylpyrone and its allies and derivatives. Accordingly, the molecular refractions of the following easily purified substances have been determined, and all data are given. Dimethylpyrone and its hydrochloride, the compound of dimethylpyrone and alcohol, diacetylacetone, pyrone, and its hydrochloride, pyromeconic acid, ethyl chelidonate, ethyl xanthochelidonate, and dehydracetic acid. Measurements were made in solution in various solvents, the specific refraction of the solute being deduced in the usual way. The possible error is estimated at about 1 per cent. When the usual formulæ, not involving quadrivalent oxygen, are used, the calculated molecular re-

fractions are in all cases considerably too low. The modified formula for dimethylpyrone proposed by Professor Collie is—



and all the other compounds examined here may be expressed by analogous formulæ. The atomic refraction of quadrivalent oxygen for the D-spectral line required by these formulæ to satisfy the experimental numbers has been found by subtraction in each case, and a good agreement between these values is obtained, the mean being 2.73.

The molecular refractions re-calculated with this number for quadrivalent oxygen agree in most cases with the experimental to within the limit of accuracy of measurement.

162. "The Alkylation of Mannose." By JAMES COLQUHOUN IRVINE and AGNES MARION MOODIE.

α -Methylmannoside has been alkylated in methyl-alcoholic solution by means of silver oxide and methyl iodide with the production of a crystalline tetramethyl α -methylmannoside, and this compound, when hydrolysed by means of dilute hydrochloric acid, was converted into tetramethyl mannose.

The alkylated sugar proved to be a colourless syrup, and when heated with methyl alcohol containing 0.25 per cent hydrochloric acid it behaved like mannose, producing only the α -modification of the corresponding mannoside. Consequently the crystalline tetramethyl α -methylmannoside was the sole product of the reaction. When the alkylation was effected by means of silver oxide and methyl iodide, however, a different result was obtained. The product was a colourless, levorotatory liquid, and this was shown to consist of a mixture of the α - and β -modifications of the fully methylated methylmannoside. The β -isomeride differs from the α -form in its levorotation and in its ready hydrolysis by means of dilute hydrochloric acid or by the action of emulsin.

163. "The Interaction of Acridines with Magnesium Alkyl Halides." By ALFRED SENIER, PERCY CORLETT AUSTEN, and ROSALIND CLARKE.

By the application of Grignard's reaction to acridine and its homologues, a series of coloured crystalline compounds has been obtained. Endeavours to replace the metal magnesium by calcium were, however, unsuccessful, for in attempting to prepare calcium alkyl and aryl halides a change resembling Fittig's reaction always occurred almost exclusively (compare Beckmann, *Ber.*, 1903, xxxviii., 904). The magnesium compounds, although readily formed, were very difficult to obtain in a pure state on account of their insolubility in inert solvents, and they were decomposed by glacial acetic acid, alcohol, and chloroform, the alcoholic solution yielding the original acridine.

On employing as solvents for the reagents ethers of high boiling-points, such as anisole and phenetole, or mixtures of either of these with ordinary ether, compounds of definite composition slowly crystallised. These products, which frequently change in colour on drying, retain variable proportions of ether, but this can be entirely removed by drying at 110–115°.

Most of the compounds examined were of the type of the diacridine hexahalides previously described (*Trans.*, 1904, lxxxv., 1199), and consist of two molecules of the base united with three molecules of the "reagent." In the case of hexamethylacridine, however, the type is that of the tetrahalides, one molecule of base combining with two of the "reagent."

164. "New Method of Determining Molecular Weights." By PHILIP BLACKMAN.

Isotonic solutions of different substances in the same

solvent having equal vapour pressures, it follows that if two solutions connected by vapour be allowed to attain equilibrium, their final volumes (v_1, v_2) will be inversely proportional to the number of dissolved molecules. This state of equilibrium is represented by the equation—

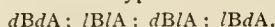
$$\frac{m_1}{m_2} = \frac{w_1}{w_2} \frac{v_2}{v_1}$$

(where m_1, m_2 , are the molecular weights of the substances, the weights, w_1, w_2 , of which are dissolved in the volumes, v_1, v_2 , of the same solvent.

The apparatus consists of two graduated test-tubes connected by a T-piece, with a bulb in each of the limbs of the U-piece. The substances are introduced into the test-tubes, the solvent added, and the solutions boiled. After a time, several readings of the volumes (v_1, v_2) are taken and the molecular weight calculated from the foregoing equations. With careful boiling, good results can be obtained in remarkably short times.

165. "Benzylphenylallylmethylammonium Compounds. A Complete Series of Four Optically Active Salts." By ALFRED WILLIAM HARVEY.

l-Benzylphenylallylmethylammonium *l*-camphorsulphonate has been prepared, having a molecular rotatory power of an equal arithmetical value to that of its dextro-isomeride, and a series of salts of the optically active base combined with optically active camphorsulphonic acids have been obtained of the type:—



The method of effecting the resolution of the iodide of the externally compensated base has been somewhat modified, whereby the difficulties previously experienced have been obviated (compare *Trans.*, 1899, lxxv., 1127, and 1901, lxxix., 828).

166. "Solid Solutions." By REINHOLD FREDERICK KORTE.

Experiments were made to determine whether barium sulphate precipitated in presence of a ferric salt forms a solid solution of ferric iron, or whether a ferrisulphate of barium is produced. The results showed that the amount of iron carried down with the barium sulphate does not increase in weight above a very small amount (about 1.3 per cent), however much of the ferric salt be present; also that there is a loss on ignition, implying the decomposition of an iron sulphate. Probably the point of saturation of barium sulphate with ferric iron is one in which the latter is present to only a minute extent, and it is also not impossible that the state of the ferric salt is that of a ferric sulphate.

The precipitation of calcium as oxalate in presence of salts of magnesium was next examined. Here, when the proportion of magnesium to calcium oxide exceeds 36MgO to 5CaO, a sudden rise in the proportion of magnesium to calcium takes place, from about 4.7 to 13.7 per cent. The magnesium is evidently present in the state of solid solution, and, although magnesium oxalate is an easily soluble salt, yet it cannot be removed from the calcium oxalate precipitate by washing.

In precipitating ferric hydroxide with ammonia in presence of a manganese salt, saturation of the ferric hydroxide with manganese takes place, when the proportion between Fe_2O_3 and MnO in solution is 5:1. A larger proportion of manganese in solution produces no change in the amount retained by the ferric precipitate, namely, 2 per cent. The absorption of small amounts of manganese by iron is nearly complete, being as much as 95 per cent. From this it follows that on re-dissolving and re-precipitating a ferric precipitate containing only a small proportion of manganese, little change in its composition takes place.

Ferric hydroxide also dissolves nickelous oxide, and a saturated solution is produced when the proportion between Fe_2O_3 and NiO in solution is 5.9 to 1.

Although manganous and nickel oxides are carried down with aluminium hydroxide, no regularity could be

observed; solid solution appears not to take place, but merely mechanical absorption by the gelatinous alumina.

Lead sulphate, precipitated in presence of other salts, does not carry down any metals in solid solution.

167. "The Bromo-derivatives of Camphopyric Acid." By JOHN ADDYMAN GARDNER.

When *cis*-camphopyric acid is treated with bromine in the presence of phosphorus pentachloride and the mixture poured into water, the chief products are *cis*-bromocamphopyric acid and *cis*-bromocamphopyric anhydride, a small quantity of *trans*-bromocamphopyric acid being also formed.

If, however, camphopyric anhydride is used instead of camphopyric acid, the chief products are *trans*-bromocamphopyric acid and bromocamphopyric anhydride, little or no *cis*-bromocamphopyric acid being produced.

trans-Camphopyric acid, treated in a similar way, using phosphorus trichloride instead of pentachloride, yields mainly *cis*-bromocamphopyric acid, a little anhydride, but no *trans*-bromo-acid.

The *cis*-acid is readily convertible into its anhydride by the action of acetyl chloride, but the *trans*-acid is not affected by this reagent. On the other hand, *cis*-bromocamphopyric anhydride, on boiling with water is converted into a mixture of *trans*-bromocamphopyric acid and decomposition products, probably of the *cis*-acid.

The bromine atom is readily replaceable. By the action of nascent hydrogen, *trans*-bromocamphopyric acid yields *trans*-camphopyric acid, whilst both *cis*-bromocamphopyric acid and *cis*-bromocamphopyric anhydride give ordinary camphopyric acid. Under the influence of alkalis, the bromine atom in both acids may be replaced by hydroxyl.

168. "The Reduction of Metallic Oxides by Aluminium Carbide." By JOHN NORMAN PRING.

Alloys of aluminium can be prepared by direct reduction of the oxide by carbon in presence of many other metals, whereas without such auxiliary metals the product consists chiefly of aluminium carbide. These considerations led to a detailed study of the reactions between aluminium carbide and metallic oxides and metals. It was found that the carbide behaves as a strong reducing agent. Up to 1400°, both the aluminium and the carbon are simultaneously oxidised, forming alumina, carbon dioxide, and the metal of the oxide. At higher temperatures, however, selective reduction becomes apparent, the reduction being more and more brought about by the carbon of the carbide the higher the temperature of reaction, the result being that alloys of aluminium and the reduced metal are obtained, the percentage of aluminium increasing with the temperature, and, in the case of iron, finally reaching the limit demanded by the equation $\text{Fe}_2\text{O}_3 + \text{Al}_4\text{C}_3 = 2\text{Fe} \cdot 4\text{Al} + 3\text{CO}$.

Calcium carbide was found to exhibit a similar behaviour, but to a less marked degree, interaction between lead oxide and excess of molten calcium carbide giving an alloy containing 2.6 per cent of calcium.

Aluminium carbide reacts with metals at temperatures above the melting-point of platinum to form aluminium alloys with liberation of free carbon; at higher temperatures, the reaction takes place with violence, and is complete.

A study of the action of metallic calcium on aluminium carbide showed that calcium carbide is formed at all temperatures above the melting-point of platinum, and as aluminium acts on calcium carbide, producing aluminium carbide, the reaction is probably reversible.

169. "The Rusting of Iron." By WYNDHAM ROWLAND DUNSTAN, HOOPER ALBERT DICKINSON JOWETT, and ERNEST GOULDING.

A detailed account is given of the investigation on the rusting of iron, an outline of which has been already published (*Dunstan, Proc.*, 1903, xix., 150).

170. "Studies in Comparative Cryoscopy. Part III. The Esters in Phenol Solution." By PHILIP WILFRED ROBERTSON.

The molecular depressions of the esters in phenol solu-

tion tend to increase with the concentration. In many instances, however, there is an initial association; that is, the molecular depression first decreases, so that under these conditions a minimum is exhibited in the molecular depression curve.

The concentration at which the minimum occurs is a characteristic for each ester, but is greater in the case of esters of high molecular weight. The initial association of these compounds becomes more rapid as the molecular weight increases.

The ethyl esters of the normal fatty acids differ from odd to even members of the series, but each division forms a perfectly definite series. Thus, in the case of the compounds with an even number of carbon atoms, the initial molecular depression reaches a maximum at the sixth member, falls to a minimum at the twelfth, and then rises to a second maximum when the chain contains sixteen carbon atoms.

The esters derived from polybasic acids are characterised by the following behaviour.

1. Their molecular depressions increase rapidly with the concentration.

2. The minimum in the molecular depression curve is not always exhibited.

3. They have extremely high initial molecular depressions.

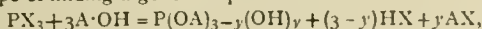
The negative "rate" of association and the abnormally high molecular depressions of the esters are probably due to the great tendency of phenol to form molecular complexes, since, in the case of the substituted phenols, thymol, guaiacol, and *o*-nitrophenol, which are not so strongly associated, these irregularities tend to disappear.

171. "The Iodides of Copper." By JAMES WALLACE WALKER and MARY VIOLETTE DOVER.

When equivalent solutions of potassium iodide and copper sulphate are mixed, the resulting precipitate seems to contain a definite polyiodide of copper mixed with the cuprous iodide, and not, as has been hitherto assumed, free iodine. Treatment of this precipitate with water gives a deep red solution, the analyses of which point to the formula CuI_4 for the solid polyiodide. From a study of the equilibrium between this solution and cuprous iodide, the authors conclude that it contains an equimolecular mixture of CuI_2 and CuI_6 . The limit of concentration of pure cupric iodide solution is almost exactly 0.1 per cent, removal of the water even in the form of ice inducing the reaction $6\text{CuI}_2 \rightleftharpoons \text{CuI}_6 + 5\text{CuI}$. Even higher polyiodides than these can be obtained from alcoholic solution.

172. "The Interaction of Alcohols and Phosphorous Halides." By JAMES WALLACE WALKER and FREDERICK MURRAY GODSCHALL JOHNSON.

The authors have studied the yield of alkyl halide obtained in the action of phosphorous chloride, bromide, and iodide on methyl, ethyl, and *n*-propyl alcohols, in the hope of finding a general equation such as—



applicable to the several cases. In this equation, X represents a halogen atom and A an alkyl group. In the production of methyl and *n*-propyl bromides, and of ethyl iodide, the value of y is 2; in the case of ethyl chloride, it is 1. In the other instances, the above equation would require to be doubled to express the results. The high degree of solubility of yellow phosphorus in methyl iodide suggested a ready method for the production of that substance in quantity. The theoretical weight of iodine is added to a 10 per cent solution of phosphorus in methyl iodide, and the equivalent amount of alcohol is slowly introduced. Enough phosphorus is then dissolved in the resultant liquid to produce again a 10 per cent solution, and iodine and alcohol are added as before. By continuing this process a large quantity of methyl iodide may be obtained in a short time, the yield being 94 per cent of the theoretical. Only 65 per cent of the theoretical yield of ethyl iodide was obtained by this method. Instead of employing the phosphorus and iodine in the ratio required

for the production of the tri-iodide, an almost equally good result is obtained by adding enough iodine to produce the penta-iodide, this compound being much more soluble than the tri-iodide in methyl iodide.

173. "The Electrical Conductivities of some Salt Solutions in Acetamide." By JAMES WALLACE WALKER and FREDERICK MURRAY GODSCHALL JOHNSON.

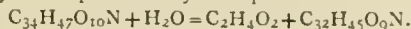
The salts examined were mercuric chloride, potassium chloride, iodide, and cyanide. Of these the first is the only normal electrolyte, the others showing a maximum of molecular conductivity at about 30 or 40 litres, which then falls to about half value on dilution. Mercuric chloride is known to give a compound with acetamide, and potassium iodide is found to yield the compound $\text{KI} \cdot 6\text{CH}_3 \cdot \text{CO} \cdot \text{NH}_2$. The migration ratio of the iodion is found to be greater than in aqueous solution, a fact which points to combination of the ions with the solvent.

174. "Contributions to Our Knowledge of the Aconite Alkaloids. Part XVI. Indaconitine, the Alkaloid of *Aconitum chasmanthum*." By WYNDHAM ROWLAND DUNSTAN and ALBERT EDWARD ANDREWS.

Indaconitine is a highly poisonous alkaloid which has been obtained from the Indian plant known as "mohri," at first thought to be the same as the European *Aconitum Napellus*, but now recognised as a distinct species, *Aconitum chasmanthum*. In this paper a full account is given of the properties of the alkaloid and of its principal salts.

Indaconitine ($\text{C}_{37}\text{H}_{47}\text{O}_{10}\text{N}$) is a crystalline alkaloid very closely resembling aconitine from *Aconitum Napellus* in its general properties, but differing, however, in its habit of crystallisation and in many of its physical properties. Most of the salts crystallise well, and are distinct from the corresponding aconitine salts. Its physiological action has been shown to closely resemble that of aconitine and pseudaconitine (Cash and Dunstan, *Proc. Roy. Soc.*, 1905).

Indaconitine undergoes hydrolysis in two stages, in the first of which an acetyl group is eliminated as acetic acid, with the formation of a base, indbenzaconine, which has not been crystallised, but furnishes crystalline salts. This hydrolysis is represented by the equation—



Indbenzaconine is practically non-poisonous. On further hydrolysis, indbenzaconine furnishes benzoic acid and pseudaconine identical with the final hydrolytic product of pseudaconitine.

Indaconitine is therefore of interest as representing a type of highly toxic alkaloid intermediate in its properties between the aconitine of the common European aconite (*A. Napellus*) and the pseudaconitine derived from the Indian aconite of Nepal. The discovery of this alkaloid and its proximate constitution has led the authors to change the formula of pseudaconitine from $\text{C}_{36}\text{H}_{49}\text{O}_{12}\text{N}$, the formula originally assigned to the alkaloid by Wright, to $\text{C}_{36}\text{H}_{51}\text{O}_{12}\text{N}$.

175. "Contributions to Our Knowledge of the Aconite Alkaloids. Part XVII. Bikhacnitine, the Alkaloid of *Aconitum spicatum*." By WYNDHAM ROWLAND DUNSTAN and ALBERT EDWARD ANDREWS.

This alkaloid, like indaconitine described in the previous communication, is highly poisonous. It has been isolated from a supposed variety of *Aconitum ferox* of India, which has now been proved to be a distinct species, *Aconitum spicatum*. The vernacular name of the plant being "bikh," the name bikhacnitine is proposed for the new base.

Bikhacnitine ($\text{C}_{36}\text{H}_{51}\text{O}_{11}\text{N}$) does not crystallise so readily as other "aconitines," and its physical properties are distinct. A number of its salts have been prepared, and most of them crystallise well. Its physiological action very nearly resembles that of the other aconitines: its toxicity towards warm-blooded animals is greater than that of either aconitine or japaconitine, but is slightly inferior to that of pseudaconitine, which is the most poisonous alkaloid of the group.

Bikhaconitine, like the other aconitines, undergoes hydrolysis in two stages. In the first of these, an acetyl group is eliminated as acetic acid, forming a new base (veratroylbikhaconine). This alkaloid does not crystallise, but furnishes crystalline salts. On further hydrolysis veratroylbikhaconine furnishes veratric acid and bikhaconine, which does not crystallise, but furnishes crystalline salts. This alkaloid differs from other "aconines" previously described.

The paper contains a full account of the properties of bikhaconitine, its salts and derivatives, and a comparison of their properties with those of the other aconitines which have been previously described. The formula of bikhaconitine differs from that of pseudaconitine by one atom of oxygen.

176. "Contributions to Our Knowledge of the Aconite Alkaloids. XVIII. The Aconitine Group of Alkaloids." By WYNDHAM ROWLAND DUNSTAN and THOMAS ANDERSON HENRY.

This paper gave a general account of the properties of the several closely allied "aconitines" which have been described in the course of the present investigation, and also of the non-poisonous alkaloids obtained from varieties of aconitine. It is pointed out that now that it has been established that closely related Indian aconites furnish similar, but nevertheless quite distinct, toxic alkaloids, it is most desirable that a similar examination should be made of the European aconites of the type of *Aconitum Napellus*. The work of Wright, Jurgens, and other chemists, as well as that of the present investigators, renders it highly probable that an examination of European plants commonly classed as *Aconitum Napellus* will reveal the presence of alkaloids very closely resembling, but yet distinct from, aconitine. The evidence already recorded goes to show that the aconitine isolated by Wright from English plants and analysed by him and others, which was described in the course of the present investigation, is a distinct substance from the aconitine of German origin which is now an article of commerce.

PHYSICAL SOCIETY.

Ordinary Meeting, November 10th, 1905,

Dr. C. CHREE, F.R.S., Vice-President, in the Chair.

A PAPER ON "The Question of Temperature and Efficiency of Thermal Radiation" was read by Mr. JAMES SWINBURNE.

It has long been known that various surfaces have different emissivities, and it is generally held that at a given temperature some bodies radiate a larger percentage of their total radiation in the form of light. This view is largely based on some experiments by Evans and Bottomley. Evans's experiments really show that if two filaments A and B of the same area but of low and high emissivities respectively are run to give the same light, the filament A of lower emissivity will give a higher efficiency, and it will give a still higher efficiency if run so as to use the same power as B. This is a natural consequence of the different emissivities, and does not at all show that A gives a higher efficiency at the same temperature as B. Prof. Bottomley's experiments are criticised on the ground that he used no photometer, and his reasoning attacked on the ground that he makes the same slip as Evans in confusing difference of emissivity with difference of efficiency at the same temperature. It is urged that a body A at the same temperature as B cannot give out radiation corresponding to a higher temperature of B; for if it could, and A and B were enclosed in a perfectly reflecting space, A would heat B to a higher temperature than A. It may be said that A can have a higher efficiency than B, not by giving out rays corresponding to B at a higher temperature, but by omitting to give some of the longer radiations that B gives. If this

were true, a hot body might be surrounded by a thin case of A lined inside with a substance which only emitted and absorbed long waves. The case would then take in long and give out short waves, though colder than the source. High efficiency or selective emissivity are always sought in polished grey, or white surfaces like flashed filaments, platinum and other metal wires and rare earths. If there were such a thing, it should be found not in white but in black bodies, as a body which is a specially good radiator of light when hot should be black when cold. Lummer's curves of the distribution of energy for a "black body" and polished platinum are compared, and show somewhat higher efficiency for platinum; but the comparison is difficult. The behaviour of flashed lamps and incandescent gas-mantles is explained by the difference of emissivity, without any need for selective emissivities.

The Secretary read a letter from Dr. J. T. BOTTOMLEY, in which he stated that the author's paper seemed to be to a large extent an attack on his work on radiation. He could not see that Mr. Swinburne had made a single experiment in support of his proposition that "in the case of pure temperature-radiation, the light efficiency is a function of the surface-temperature only." No amount of discussion such as the author asked for could do anything to prove or disprove this proposition. He failed to see that the author had worked out any logical proof of the proposition. The author had assumed that he (Dr. Bottomley) was incapable of matching the light-giving properties of two platinum strips placed side by side and properly arranged for this sort of comparison. The matching is exactly the same in principle as in shadow photometry, and in all the cases cited in the paper to which Mr. Swinburne takes exception, Dr. Bottomley's determinations agreed with those of his assistant, Mr. Evans.

Dr. J. A. HARKER expressed his interest in the paper, and said that the question of radiation was of practical importance in the measurement of high temperatures by electrical resistance methods. He asked if two platinum thermometers, one bright and the other blackened, but identical in other respects, were transferred from an ice-bath into a sulphur-bath, would the final temperatures of the two thermometers be the same, and also would the thermometers approach their final temperatures at the same rate?

Prof. H. L. CALLENDAR, referring to Dr. Harker's questions, stated that if the sulphur-bath was in an isothermal enclosure, the two wires would reach the same ultimate temperature although the blackened one would reach it quicker. The difference, however, would be small. With fine wires the loss of heat by conduction through the gas is more important than the radiation loss. The loss by radiation is proportional to the surface, but the loss by conduction is not, and it therefore becomes relatively more and more important with the fineness of the wire. With regard to the action of incandescent mantles, he thought the author's theory was reasonable and satisfactory.

Mr. MAURICE SOLOMON said he did not agree with Mr. Swinburne's contention that in the case of solids there was no such thing as selective emissivity, but that all bodies at the same temperature radiated light of the same efficiency. Selective emissivity existed in the case of incandescent vapours, and if it was consistent with the laws of thermodynamics in such a case, it could not be inconsistent in the case of an incandescent solid. With reference to the incandescent mantle, the explanation put forward by the author did not seem satisfactory. It was difficult to believe that the very small differences in colour between a thoria, a thoria-ceria, and a ceria mantle could account for the enormous differences in their candle powers.

Prof. W. E. AYRTON referred to experiments which he had carried out which tended to show that the temperature of a Bunsen flame was lowered by an incandescent mantle. He had also found that small pieces of mantle heated in a platinum boat to various temperatures just below the melting-point of platinum never looked brighter than the

platinum. If, however, a small hole was made in the bottom of the boat and coal-gas passed in, the mantle immediately became brilliant.

Mr. SWINBURNE, replying to Dr. Bottomley, said that his main argument was that he had not made experiments. In the investigation of a question such as that considered in the paper, it was possible to prove much by means of experiment, but it was also possible to attack the problem by thermodynamic reasoning. He expressed his interest in the fact that Prof. Callendar had referred to his views as reasonable.

Mr. T. H. BLAKESLEY read a "Note on Constant-deviation Prisms."

It appears that any prism of three faces can be made to give a spectrum in which the light, that occupies the centre of the field of view of the telescope at any moment, has undergone passage through the two refracting surfaces of the prism in such a way that its original angle of incidence is equal to its final angle of emergence. This condition, which in the ordinary employment of the prism is associated with minimum deviation, must be described as isogonal passage, the property which has the minimum value being not the deviation, but the rate of passage across the field of view for a given motion of the prism, to which alone in these instruments motion has to be given to bring different parts of the spectrum into the field, the telescope and collimator both remaining fixed. If any triangle having the angles α , β , γ is adopted as the shape of a prism, the telescope must be set to make one of these angles, say γ , with the line of the collimator. Then the prism being placed in the region between them, a position can be found so that any ray selected will be refracted through one of the sides containing the angle γ , reflected at the side opposite γ , and finally refracted through the remaining side containing γ . On emergence it will be parallel to the telescope, and its passage through the refracting faces will be isogonal. The prism will affect the light to the same degree as one used in the ordinary way, of refracting angle $\beta - \alpha$, would do. The sine of the angle of original incidence is equal to $\mu \cdot \sin(\beta - \alpha)/2$ for every ray occupying the centre of the field of view.

If the prism is turned over but the same angle γ employed, the telescope will remain unaltered but the spectrum will run in an opposite direction to the first. If n similar prisms are piled one upon another, the diameter of the telescope and collimator being large enough to embrace them all, n different parts of the spectrum may be brought into coincidence at the centre of the field of view. Thus such prisms afford an excellent mode of mixing colours. Mr. Blakesley showed the case of two prisms in which the spectra ran in different directions. The top prism was slightly tilted by the insertion of a small piece of silver paper between the prisms. By this means one of the spectra was shifted upwards by a small amount, and one could see in the telescope a band, at top and bottom, of the component colours, and in the centre a band of the resulting colours. It was suggested that spectroscopes on this plan could be advantageously employed in measuring the motion in the line of sight of heavenly bodies, as a line brought into coincidence with itself for a terrestrial source in the two spectra would, in the case of such motion, split up into two moving different ways in the field of view. It was also explained how such prisms could be placed in trains for increased dispersion.

ROYAL SOCIETY OF NEW SOUTH WALES.

General Monthly Meeting, September 6th, 1905.

H. A. LENEHAN, F.R.A.S., President, in the Chair.

The following paper was read:—

"Reinforced Concrete" (Paper III.). By Professor W. H. WARREN, Wh.Sc., M.Inst.C.E., M.Am.Soc.C.E., Challis Professor of Engineering, University of Sydney.

The following matters were dealt with:—

a. The adhesion of cement mortar and concrete to steel.
b. The experimental determination of the neutral axis in a plain concrete, and also in a reinforced concrete beam, and the curves of strain for loads increasing from zero to the load producing fracture; the determination of the true form of the stress curve from the actual strain curve in a plain and in a reinforced concrete beam.

c. The safe working stresses and the fundamental equations recommended for the design of reinforced concrete structure.

d. The adhesion of cement mortar and concrete to the steel reinforcement was determined by pulling out specially prepared bars of Bessemer steel from prisms 12 inches long $\times$ 4 inches $\times$ 4 inches cross section, by means of a testing machine.

Pounds per sq. in.

1. With steel bars having the natural skin on, after forty-five days' hardening in air .. 198
2. With the skin removed and the bars polished, after forty-five days' hardening in air 125
3. With the skin removed (as in 2), but hardened in water, after forty-five days . 185

The experimental determination (b) was made in a special form of Buckton testing machine, with two hydraulic presses for applying the loads at the ends of the beams tested. Ten beams 72 inches long were tested on supports 40 inches centre to centre, with two overhanging portions each 16 inches long. The apparatus for measuring the lengthening and shortening of the beam between the supports over a length of 40 inches, consisted of eight Marten's mirror extensometers, with a corresponding number of scales and telescopes arranged at different positions in the depth of the beam. The extreme fibre strains were determined by means of four Marten's sector extensometers, and the deflections with dials. The mirror extensometers read accurately to 1/10000 of a millimetre, and it will be observed that the bending moments and corresponding stresses between the supports over a length of 40 inches are constant (neglecting the effect of the weight of the beam itself). Four reinforced beams were exactly alike in composition, age, and reinforcement, and the mean deformations, which differed very slightly from the corresponding individual deformations, were plotted. The strain curves proved that a plane section before flexure is not a plane section after flexure, and that the deviation from the plane is greater as the bending moment increases. Again, the neutral axis moves from the centre of the beam towards the compression side as the bending moment increases. The stress curves determined from the strain curves are fairly straight for a bending moment of about one-third of that producing fracture, but they are curved for greater bending moments approximating closely to parabolas just before fracture. The stress curves determined from the tests of the other reinforced concrete beams confirm these results completely. In the plain concrete beam, without reinforcement, the strain curves were approximately straight lines, and the stress curves deduced from them were curved more on the tension than on the compression side, but in both they approximated closely to parabolic curves; the neutral axis also moved 0.8 of an inch towards the compression side as the bending moment was increased.

In regard to the application of these conclusions to the practical design of reinforced concrete structures, it appears desirable to neglect the tensile stress in the concrete, as it contributes little to the moment of resistance of the beams.

Prof. WARREN read some notes on hardness of different metals, and exhibited a Sclerometer for testing same.

Mr. LENEHAN exhibited and explained a chart showing drift of the s.s. *Pilbarra*, after losing her propeller blades.

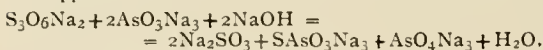
CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

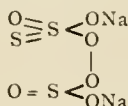
Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxviii., No. 13, 1905.

Simple Method of Preparing Pure Monoethyl-aniline from Technical Monoethyl-aniline.—G. Blume and H. Klöffler.—If to 97 grms. of the technical product 65 c.c. of concentrated hydrochloric acid is added, a crystalline chlorhydrate separates out after a short time. By leading gaseous hydrochloric acid into the mother-liquors additional small quantities of chlorhydrate are obtained. The total amount is 101 grms., corresponding to a yield of about 80 per cent. The chlorhydrate may then be decomposed by caustic soda, and the oil driven over by steam, dried, and distilled. The distillate is pure monoethyl-aniline.

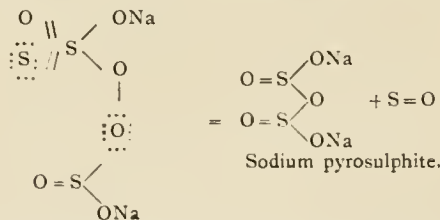
Reduction of Trithionates to Sulphites by Arsenites and Stannites.—A. Gutmann.—When tertiary arsenite acts upon trithionate, sulphite, monosulphoxyarsenate and arsenate are formed, although the formation of the last named was not to be expected, judging from the results of previous researches. Quantitative experiments show that one molecule of trithionate yields one molecule of arsenate, and accordingly gives off one atom of oxygen. The equation appears to be—



The formula of the trithionate is—



which breaks up as follows when treated with a reducing agent:—

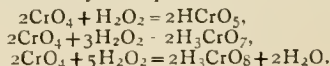


Sodium stannite reduces trithionate in alkaline solution to sulphite, yielding also sulphostannate and stannate. Dithionates do not react with arsenites and stannites, being very stable towards these reagents.

Titanium Trichloride in Volumetric Analysis.—E. Knecht and Eva Hibbert.—The powerful reducing action of titanium trichloride may be employed for the volumetric determination of coloured organic bodies, which form colourless leuco bodies when two atoms of hydrogen are added to the molecule. The coloured substance acts as its own indicator for the titration. To get accurate results the titration must be performed in the absence of air, owing to the fact that the leuco compounds are easily oxidisable. If pure indigotin is sulphonated and the di-sulpho acid is diluted with water and titrated with titanium trichloride in an atmosphere of carbon dioxide after addition of Seignette's salt, a very sharp end reaction occurs, the blue colouration suddenly changing to orange-yellow. The results thus obtained agree very well with the theory. With impure specimens of indigo it is best to remove all impurities from the sulphuric acid solution by neutralising with calcium carbonate. Eosine A, rhodamine B, pararosaniline

chlorhydrate, pararosaniline trisulphonic acid, malachite green, and crystal-violet are among the dye-stuffs which give satisfactory results when titrated thus with titanium trichloride. In the case of the first two, some alcohol must be added, otherwise the solution becomes turbid on titration, probably in consequence of the separation of leuco compound, and the end reaction is not sharp. From these results it appears that titanium trichloride may be used for the quantitative determination of some of the most important basic dye-stuffs (and in some cases of their sulphonated derivatives), and that it gives more accurate results than any other method. If the titanium chloride solution is ready prepared, the determinations (except in the case of indigo) can easily be performed in twenty to thirty minutes. If a dilute solution of the trichloride is added slowly to a solution of hydrogen peroxide a deep orange-yellow colouration is produced, and this reaction may be used for the quantitative determination of hydrogen peroxide. If more trichloride is added the colour of the solution gradually fades, after it has reached a maximum, and disappears altogether as soon as the reduction of the peroxide and the oxidation of the trichloride are complete. For this determination the titanium salt must be free from iron, and the technical product cannot be used. Other inorganic substances to which the authors have applied the same method of determination are ammonium persulphate and metallic tin.

Perchromic Acids.—E. H. Riesenfeld.—If an alkaline aqueous solution of chromic acid is oxidised by means of 30 per cent hydrogen peroxide, red-brown crystals of a salt of the acid H_2CrO_8 are obtained on cooling. If the solution is acidified before the addition of the peroxide blue crystalline salts are obtained, and it is immaterial whether we employ a strong or weak acid (e.g., hydrochloric or acetic acid) or an acid of medium strength (e.g., oxalic acid). These blue salts are much less stable than the red, and are probably identical with the substances which Wiede prepared by adding an alcoholic alkali solution to ethereal perchromic acid solution at a low temperature (-5°). Wiede ascribed to them the formulae KH_2CrO_7 and $(\text{NH}_4)_2\text{H}_2\text{CrO}_7$. If instead of alkali pyridine is added to a solution of chromic acid anhydride in water, which is then oxidised by means of hydrogen peroxide, a blue crystalline substance of the formula PyHCrO_5 separates out, a derivative of the acid HCrO_5 . Moreover, if the same very dilute solution used to prepare $(\text{NH}_4)_3\text{CrO}_8$ is allowed to stand at the temperature of the room, after twelve to twenty-four hours crystals of the composition $\text{CrO}_4 \cdot 3\text{NH}_3$ separate out, which resemble the crystals of $(\text{NH}_4)_3\text{CrO}_8$ very strongly in appearance, though they are somewhat darker in colour. If a paste is made of $(\text{NH}_4)_3\text{CrO}_8$ and water and acids are added to it, oxygen is given off, and the salt $(\text{NH}_4)_2\text{H}_2\text{CrO}_7$ separates out. When an excess of pyridine is added to a paste either of $(\text{NH}_4)_3\text{CrO}_8$ or $(\text{NH}_4)_2\text{H}_2\text{CrO}_7$, the salt PyHCrO_5 is obtained, and from all three salts, $(\text{NH}_4)_3\text{CrO}_8$, $(\text{NH}_4)_2\text{H}_2\text{CrO}_7$, and PyHCrO_5 , an excess of ammonia gives $\text{CrO}_4 \cdot 3\text{NH}_3$, the most stable of all the higher oxidation products of chromium. All these reactions may be explained by supposing that hydrogen peroxide is either taken up or given up, as represented by the equations:—



All these compounds give a violet-blue colour if their aqueous solutions are treated with ether and acids are added, the tint varying from a reddish violet to a deep indigo blue, according to the amount of oxygen in the chromium compound and the concentration of the acid; the strongly acid solution of the highest oxidation product gives the deepest blue colour. As these substances are formed on the oxidation of aqueous chromic acid solutions, both from the ethereal and aqueous solutions, we may assume that in the blue ethereal so-called "perchromic acid solution" a mixture of these substances is present, and not a single

substance. The empirical formula of these substances may be expressed by $2\text{CrO}_4 + x\text{H}_2\text{O}_2$, the acids of the salts known at present being these for which $x = 1, 3, \text{ and } 5$. Compounds derived from an oxide (or acid anhydride) Cr_2O_7 do not produce a blue colouration in the ether, and thus the blue colour is due to the oxide CrO_4 alone and to its derivatives.

Complex Molybdenum Rhodanides.—J. Sand and O. Burger.—If to an acidulated solution of ammonium molybdate and rhodan ammonium a reducing agent is added, a dark reddish brown colouration is produced. On addition of ether or amyl alcohol and evaporation of the solvent, a semi-solid mass is obtained. If tertiary bases are added to the ethereal or (amyl) alcoholic extract from the acid solution, well defined crystalline compounds are obtained. For instance, pyridine yields, according to experimental conditions, either brownish red crystals of $\text{Mo}(\text{SCN})_4\text{Py}_2$ (I.) or yellow tablets of $\text{Mo}(\text{SCN})_4\text{Py}_4 + 2\text{PyHSCN}$ (II.). The composition of pyridine compound I. shows that the red rhodanide, easily soluble in organic solvents, is a derivative of tetravalent molybdenum; and the behaviour of pyridine salt II. seems to show that the molybdenum is hexavalent. Four rhodan-residues are precipitated from it by means of silver nitrate. Thus the constitutional formula of salt II. appears to be—



or else $\left[\begin{smallmatrix} \text{iv. (PyHSCN)}_2 \\ \text{Mo Py}_4 \end{smallmatrix} \right] (\text{SCN})_4$. The brown pyridine salt I. must then be given the formula $\left[\begin{smallmatrix} \text{Mo Py}_2 \\ (\text{SCN})_4 \end{smallmatrix} \right]$.

The oxidation products of these substances cannot be determined by titration with permanganate, because of the SCN residue they contain. The brown molybdenum dipyridine tetra-rhodamide I. was therefore converted into yellow prisms of $\text{MoCl}_4.6\text{PyHCl}$ by the action of hydrochloric acid in acetone solution. This chloride is soluble in water, and all the chlorine in a solution of it in nitric acid can be precipitated as silver chloride.

MEETINGS FOR THE WEEK.

MONDAY, 27th.—Society of Arts, 8. (Cantor Lectures). "Measurement of High Frequency Currents and Electric Waves," by Dr. J. A. Fleming, F.R.S.

WEDNESDAY, 29th.—Society of Arts, 8. "The British Association in South Africa," by Sir William H. Freese, K.C.B., F.R.S.

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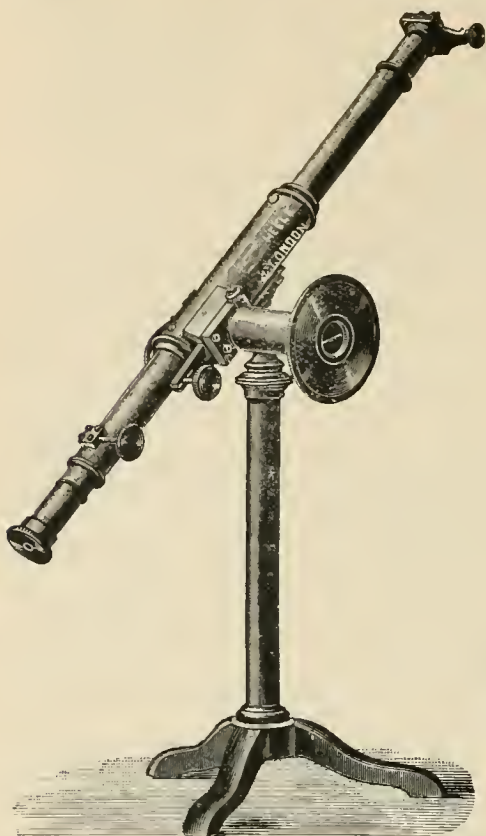
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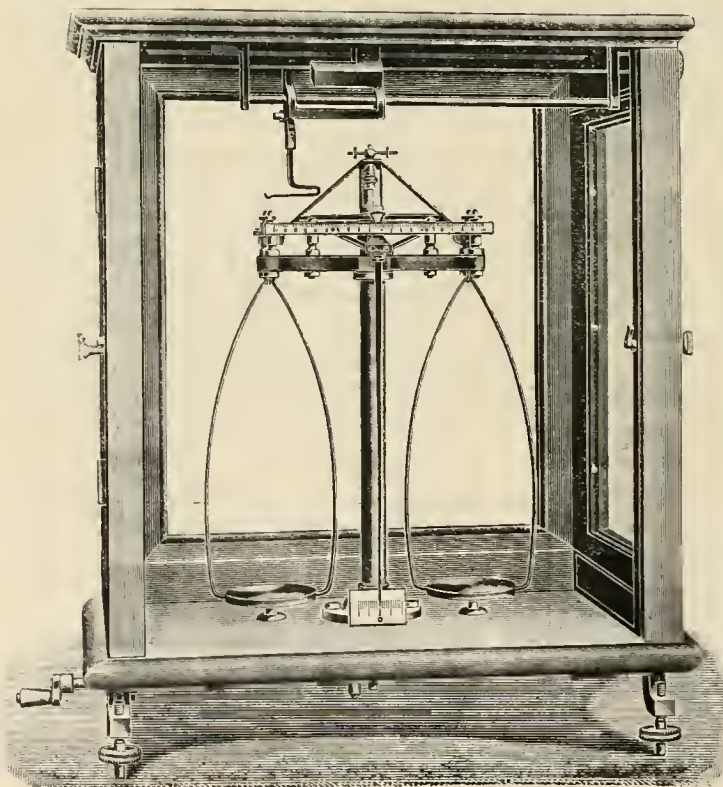
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A NEW RADIO-ACTIVE ELEMENT WHICH EMITS THORIUM EMANATION.

By O. HAHN.

IN March, 1905, a preliminary communication by the author under the above title was brought before the Royal Society of London by Sir William Ramsay (*Proc. Roy. Soc., A*, lxxvi., 115; *Zeit. Phys. Chem.*, 1905, li., 717). I now propose to give briefly the results of further work on the same subject. These results confirm and supplement the preliminary communication.* The name radio-thorium is proposed for the constant strongly radio-active element, which in all probability forms the active constituent of thorium, which is in itself perfectly inactive. As regards its preparation from the barium-radium mixture, it was first collected in the more soluble liquors of the fractionation, and then precipitated together with some iron by means of ammonia. It thus appeared that this fractionation method, even after it had been applied repeatedly, did not lead to the desired result. Another method of separation was therefore sought; a drop of iron chloride solution was added to each separate radium fraction, which all contained radio-thorium as well, and then the iron was precipitated by means of ammonia. In this case also no quantitative separation from radium was effected; moreover, some radium was always to be found in the ammonia precipitates.

A separation by means of sulphuric acid was not possible either, as the radio-thorium would be carried down also.

By repetition of the methods stated, however, a satisfactory separation of the radio-thorium from the radium could be effected.

Then a greater difficulty lay in the concentration of the radio-thorium precipitates. Chemically these consist principally of iron and an element belonging to the rare earths, whose nature is not yet known. It does not seem to be thorium.

The method first employed to separate the radio-thorium from the greater part of the iron by means of ammonium oxalate or oxalic acid is not suitable, because the further working up of the oxalates—which naturally amount only to some m.grms.—is difficult to perform without loss. Single precipitations are not generally successful, and a fractionation mechanism must always occur. The "carbonate separation" gives fairly good results. The acid solutions were precipitated with ammonium carbonate in excess in the cold. On boiling the filtrate some basic carbonate separated out; this was relatively more strongly active than the carbonate precipitated in the cold. Shortly after the precipitation the activity relations are indeed somewhat altered, as thorium X is concentrated more in the first precipitate, and in the second precipitate it has to be formed anew. In this case also many repetitions are prevented, owing to the fact that the quantities rapidly become too small. Up to the present, by far the strongest product obtained was 10.9 m.grms. of a dirty brownish substance which was by no means elementary. It gives off almost 700,000 times as much emanation as an equal weight of ordinary thorium under the same conditions; the 10.9 m.grms. thus correspond in activity to about 71 k.grms. of thorium of ordinary activity. Besides this quantity, smaller quantities of less activity are present; but it is hardly possible with the material obtainable to get a greater concentration or to obtain more.

* A more complete description of the preparation and properties of the active substance appeared in the October number of the *Zeitschrift für Radioaktivität und Elektronik*. The discussion of the name radio-thorium will also be found there.

As regards the properties of radio-thorium, the name expresses that it possesses the radio-active properties of thorium. It was already apparent from the constancy of the activity that something besides thorium X is present. A preparation kept for more than half a year showed no trace of decrease of activity. The activity of thorium X would have fallen to half its value in four days. The first decomposition product of radio-thorium is precisely this thorium X. The latter may be separated from the constantly active part in the usual way by precipitation with ammonia. The time in which the thorium X sinks to half its value was found to be 4.1 days. The decay constant λ is 196×10^{-8} . The correct number may differ from this within narrow limits; for reasons given at the place cited, the measurements which have been taken are not entirely free from objection. Rutherford and Soddy give the time as four days.

The emanation was investigated most thoroughly. As the mean of a great number of emanation measurements agreeing very well among themselves, with the most varied radio-thorium preparations the value 1.3×10^{-2} was found for λ ; thus the emanation sinks to half its value in 53.3 seconds. For thorium emanation other investigators have found 51.2 and 54 seconds. The extraordinarily large quantity of emanation naturally produces very characteristic phenomena in the dark room; these phenomena are externally hardly distinguishable from those exhibited by actinium emanation. If the little glass vessels containing the 10.9 m.grms. of the substance on a filter wrapped in paper are opened, the emanation spreads itself in clouds over the zinc sulphide screen, and naturally on blowing the characteristic luminescence disappears. It is noteworthy that the emanation rises, and does not sink, as was supposed. If we do not wish to abandon the usual idea that all radio-active elements are those with high atomic weights, no explanation of this can be given; a measurably higher temperature than the surroundings could not be established. The actinium emanation, moreover, shows this property very clearly, while the radium emanation, which is visible even without a screen, undoubtedly behaves like a heavy gas.

As the thorium emanation always needs two to three minutes to collect, after blowing away the emanation the vessel must be closed again for two or three minutes in order to reach the maximum of luminous effect.

According to Rutherford's researches, solid thorium compounds behave very differently as regards their power of emanation; specimens "de-emanated" by ignition give off only very little emanation, and in this respect closely resemble radium, which in the solid state yields only very small quantities of radium emanation. The agreement of radio-thorium with "ordinary" thorium is shown here also. The moving emanation is no longer to be seen after strongly igniting my radio-thorium preparations, but the direct luminescence action on the zinc sulphide and platinum screens is considerably increased. All the induced activity is stored up in the preparation; the total activity is thus greater after ignition than before. As the thorium emanation is condensed by liquid air, by immersion in liquid air we obtain for a moment the same result as by ignition. The emanation condenses in the preparation, the induced activity accumulates till equilibrium is reached, and the preparation becomes more strongly active. After being taken out it again becomes more feeble in the same proportion. Radio-thorium itself is not luminescent, but the glass vessels in which a very strong preparation is kept show to an experienced eye distinct fluorescence in the dark. Just as with actinium or Giesel's emanium, the strong radio-thorium preparations make objects which are brought close to them strongly radio-active. If some paper is introduced into the glass vessel which contains the 10.9 m.grms. of the strongest substance, the paper after some hours shows very powerful luminescent action on the screen. This induced activity on the paper naturally cannot be indefinitely increased; if radio-active equilibrium is produced it remains constant as

long as it is in the neighbourhood of the preparation. If it is removed the induced activity naturally diminishes. The so-called scintillation of the α -rays may be seen vividly with objects thus made active by induction.

To measure the decrease of the induced activity three different methods of preparation were used. The first method was that frequently employed formerly, viz., concentration on the negatively electrified rod or wire.

A second method of preparation often used in this work was the condensation of the emanation by means of liquid air in a glass spiral, solution of the induced activity in dilute acid, and evaporation on a clock glass or in a small dish.

The simplest method is that already touched upon above:—An object is brought into the neighbourhood of the strong preparation; after a day it is removed, and the decrease is measured in the electroscope or electrometer. One of the latter is naturally always necessary for the quantitative measurements. As the mean of several series of measurements the decay constant $\lambda = 1.82 \times 10^{-4}$ was found. The time in which the half value is reached amounts to 10.6 hours; formerly eleven hours was mostly assumed for this value, but more recently 10.6 seems to have been found by another investigator also. The splitting up of induced thorium activity into thorium A and thorium B recently performed by two workers is naturally not affected by it (J. M. W. Slater, "Inducirte Aktivität des Thoriums," *Chem. Centrall.*, 1905, i., 1629; W. von Lerch, *Ibid.*; *Ber. d. Wiener Akad.*, March 2, 1905).

As yet not much is known concerning the chemical properties of radio-thorium. The smallness of the quantities available render its investigation very difficult, perfectly quantitative precipitations of the activity are never effected, and many chemical operations may therefore easily produce a very considerable "dilution" of the substance. The reactions of radio-thorium appear to be those of the rare earths, as was to be expected. But whether radio-thorium behaves chemically exactly like radium is very doubtful, and some phenomena argue against it.

In all chemical experiments we must take into account thorium X, which under some circumstances causes deviations. Therefore the measurements must always be performed at least twice at different times. The fact that radio-thorium is often carried down by all precipitates in fairly considerable quantity may easily lead to errors as regards chemical relationships.

The reasons that argue in favour of radio-thorium being the radio-active constituent of thorium, which is itself inactive, are more fully discussed elsewhere (*cf.* also Sackur, *Ber.*, 1905, xxxviii., 1756); they led also to the choice of name. The occurrence and behaviour of radio-thorium seem to show the possibility of its being the first slow decomposition product of thorium. Between thorium and radio-thorium there would thus exist a genetic connection similar to that which exists between uranium and radium, and which has recently been proved experimentally by Soddy's investigations (*Phil. Mag.*, [6], ix., 768; *cf.* Boltwood, *Am. Journ. Sci.*, [4], xx., 239).—*Berichte*, 1905, xxxviii., 3371.

SOME OBSERVATIONS ON COLUMBIUM.*

By ROY D. HALL and EDGAR F. SMITH.

(Continued from p. 243).

Behaviour of Solutions of the Double Fluorides of Columbium and of Titanium with a variety of Bases.

EXCESS of sodium hydroxide was found to precipitate titanium completely from a solution of potassium-titanium fluoride, while with potassium-columbium oxyfluoride it gave a precipitate soluble in slight excess, but again insoluble and separating in a crystalline form from a large

excess of the sodium hydroxide. The precipitate formed in the case of the titanium was insoluble in water, while, in the case of columbium, the crystalline deposit was completely soluble in hot water. It was hoped that this difference of behaviour might afford a means of separating these two elements. To test this, experiments were tried as follows:—

1. 0.0600 grm. of $K_2CbOF_5 + H_2O$, containing 0.4272 grm. of Cb_2O_5 , and 1.1600 grm. K_2TiF_6 , containing 0.3753 grm. of TiO_2 , were dissolved in 200 c.c. water, brought to boiling, and an excess of sodium hydroxide added. The precipitate which formed was partly crystalline and partly flocculent. The solution was allowed to stand over night. The precipitate was filtered out, drained, and washed back into a platinum dish. It was covered with 200 c.c. of water, brought to boiling, filtered hot, and washed with hot water. The filtrate, which should contain most of the columbium and none of the titanium, was brought to boiling, and sulphuric acid and ammonium hydroxide added. The hydrate obtained was ignited to oxide and weighed 0.1640 grm. It was found to contain 0.0117 grm. of TiO_2 . The titanium content was determined colorimetrically by fusing with potassium acid sulphate, dissolving the fusion in oxalic acid, and comparing the colour developed with hydrogen peroxide with that of a titanium solution of known strength in oxalic acid.

Part insoluble—0.2749 Cb_2O_5 , 0.3636 TiO_2 .

$TiO_2 \cdot 4Cb_2O_5$, soluble portion; $Cb_2O_5 \cdot 4TiO_2$, insoluble portion.

2. A mixture containing 0.1270 grm. K_2TiF_6 , or 0.0423 grm. TiO_2 and 2.5280 grms. $K_2CbOF_5 \cdot H_2O$, or 1.1376 grms. Cb_2O_5 , was treated as above. The precipitate was nearly all crystalline. That part of it insoluble in water weighed 0.0470 grm. and contained 0.0074 grm. TiO_2 , leaving 0.0349 grm. of TiO_2 in solution (by far the greater quantity).

3. 0.2830 grm. K_2TiF_6 , containing 0.0943 grm. TiO_2 , and 2.7040 grms. $K_2CbOF_5 \cdot H_2O$, containing 1.2168 grms. Cb_2O_5 , were treated as before. The precipitate was chiefly crystalline. A small part of it was flocculent. The part insoluble in water weighed 0.0740 grm. and contained 0.0148 grm. TiO_2 , showing that 0.0795 grm. TiO_2 went into solution and would be found with the bulk of the columbium.

4. 0.6790 grm. K_2TiF_6 , containing 0.2263 grm. TiO_2 , and 2.2530 grms. $K_2CbOF_5 \cdot H_2O$, containing 1.0139 grms. Cb_2O_5 , were treated as before. The precipitate contained a considerable amount of flocculent material. The part insoluble in water weighed 0.1720 grm. and contained 0.0710 grm. TiO_2 , leaving 0.1553 grm. of TiO_2 in solution.

The action of potassium hydroxide was also tried. It gave a precipitate with columbium, soluble in an excess and re-precipitated by greater excess. When the solution was evaporated, pearly plates of potassium columbate separated out. With a solution of K_2TiF_6 a heavy precipitate was obtained, but the filtrate gave a slight test for titanium.

1.3130 grms. K_2TiF_6 , containing 0.4377 grm. of TiO_2 , and 1.0060 grm. $K_2CbOF_5 \cdot H_2O$, containing 0.4467 grm. Cb_2O_5 , were dissolved in 200 c.c. of water and the solution brought to boiling, when an excess of potassium hydroxide was added. The precipitate obtained weighed 0.5900 grm. after ignition. The filtrate gave a very pronounced test for titanium.

Solutions of K_2TiF_6 and K_2CbOF_5 were studied with various organic bases in the hope that differences of behaviour might present themselves which would lead to a quantitative separation of these two elements. (See Table).

The behaviour of the bases which react with the above solutions of titanium and columbium may be divided into the following classes:—

1. Those which precipitate the titanium completely, and while they precipitate the columbium dissolve it upon the addition of an excess of the reagent to form columbates.

* *Proceedings of the American Philosophical Society*, 1905, xlv., p. 177.

Reagent.	Solution of K_2TiF_6 .	Solution of $K_2C_2O_4$.
1. Monomethylamine	Precipitation complete.	Precipitate soluble excess.
2. Dimethylamine	" "	" "
3. Trimethylamine	" "	" "
4. Tetramethylamine	" "	" "
5. Monoethylamine	" "	" "
6. Diethylamine	" "	" "
7. Triethylamine	" "	Precipitate by large excess; insoluble excess; difficultly soluble in water.
8. Dipropylamine	" "	Precipitate soluble excess.
9. Amylamine	" "	" "
10. Isobutylamine	" "	" "
11. Allylamine	" "	" "
12. Ethylenediamine	" "	" "
13. Propylenediamine	" "	" "
14. Butylenediamine (secondary)	" "	" "
15. Butylenediamine (normal)	" "	" "
16. Hexylamine	" "	" "
17. Benzylamine	" "	" "
18. Benzylmethylamine	" "	" "
19. Piperidine	" "	" "
20. Camphylamine	" "	Precipitate slightly soluble excess.
21. Dibenzylamine	" "	Precipitation complete.
22. Pyridine	" "	" "
23. Di-isobutylamine	" "	" "
24. Tripropylamine	" "	" "
25. Diamylamine	" "	" "
26. Heptylamine	" "	" "
27. Toluylenediamine (meta)	Partial precipitation.	" "
28. Picoline	" "	" "
29. Tri-isobutylamine	Slight precipitation.	Precipit. nearly but not quite complete.
30. Bornylamine	" "	Precipitation not complete.
31. Aniline	Precipitation not complete.	Precipitation heavy, but not complete.
32. Toluidine (<i>m</i>)	Slight precipitation.	" "
33. Monomethylaniline	Slight precipitation after 24 hours.	" "
34. Mono-ethylaniline	Slight precipitation on standing.	Precipitation slow; incomplete.
35. Isoquinoline	" "	Precipitation heavy; incomplete.
36. Quinoline	" "	Precipitation nearly complete.
37. Hexamethylenetetramine	" "	Precipitation heavy; incomplete.
38. Bromaniline (<i>m</i>)	No precipitation.	Slight precipitation on standing.
39. Chloraniline (<i>o</i>)	" "	" "
40. Dichloraniline	" "	" "
41. Diethylaniline	" "	" "
42. Chloraniline (<i>p</i>)	" "	" "
43. Dimethylaniline	" "	" "
44. Xylidine (<i>p</i>)	" "	Precipitation slow; incomplete.
45. Xylidine (<i>o</i>)	" "	" "
46. Xylidine (<i>m</i>)	" "	" "
47. Tetrahydroquinoline	" "	Slight precipitation on standing.
48. Benzylaniline	" "	No precipitation.
49. Diphenylamine	" "	" "
50. Tribenzylamine	" "	" "
51. Naphthylamine (<i>8</i>)	" "	" "
52. Naphthylamine (<i>6</i>)	" "	" "
53. Nitronaphthalene	" "	" "
54. Bromphenylhydrazine	" "	" "
55. Nitrophenylhydrazine	" "	" "
56. Benzidine	" "	" "
57. Nitraniline (<i>o</i>)	" "	" "
58. Nitraniline (<i>p</i>)	" "	" "
59. Nitraniline (<i>m</i>)	" "	" "
60. Diphenyl	" "	" "
61. Diphenyl carbonate	" "	" "
62. Methyl carbonate	" "	" "
63. Ethyl carbonate	" "	" "
64. Piperine	" "	" "
65. Monochlorhydrin	" "	" "
66. Trichlorhydrin	" "	" "
67. Dibromhydrin (<i>3</i>)	" "	" "
68. Nitrosodipropylene	" "	" "
69. Nitrosodiethylene	" "	" "
70. Nitrosodimethylene	" "	" "
71. Succinimide	" "	" "
72. Methyl diphenylamine	" "	" "
73. Tetranitromethylaniline	" "	" "
74. Bromaniline	" "	" "

This class, while showing pronounced difference of behaviour, is useless as a means of separation, for upon treating a solution containing both titanium and columbium with one of these reagents the titanium was found both in the soluble and in the insoluble portion. Columbium was also found in the titanium precipitate. The probable explanation for this is that a columbate was formed which dissolved the freshly precipitated titanium hydrate to a salt of a complex titanocolumbic acid, which was soluble, and also a small amount of an acid salt or a free acid containing an excess of titanium, which was insoluble.

2. To the second class of reagents belong those which precipitate the hydrates of the two elements, and are not sufficiently basic to dissolve the columbium hydrate and form columbates. Those reagents which are sufficiently basic to completely precipitate the columbium are strong enough to partially precipitate the titanium. Quinoline seemed the most promising of all the reagents which were tried.

3. Those reagents which gave only a partial precipitation with columbium and no precipitation with titanium solutions did not precipitate columbium hydrate free from titanium, from a solution containing both titanium and columbium. The hydrate precipitated always gave a strong test for titanium after dissolving it in oxalic acid. This may have been due in part to the extreme difficulty encountered in washing the precipitate free from mother-liquor.

4. The remaining reagents precipitated neither titanium nor columbium.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FROM THE 1ST TO THE 21ST OF OCTOBER, 1905.

By SIR WILLIAM CROOKES, F.R.S.,
and
SIR JAMES DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, November 9th, 1905.

SIR,—We submit herewith, at the request of the Metropolitan Water Board, the results of our analyses of the 144 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the Metropolitan Water Board taking their supplies from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from October 1st to October 21st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 144 samples examined by us during the month, all were clear, bright, and well filtered.

Again we have to record a deficit of rain at Oxford. The rainfall registered during October is 1.40 inches. The average rainfall is 2.76 inches; thus we have the rather large deficit of 1.36 inches, which, if added to the previous one of 2.34 inches, makes a total deficit of 3.70 inches for the first ten months of this year, or 17.7 per cent on the thirty-five years' average.

TABLE A.—Rainfall in Inches at Oxford, Month by Month, during the Year 1905.

	Actual fall.	Mean of 35 years.	Difference from the mean.	
	Inches.	Inches.	Inches.	Inches.
January ..	0.78	2.08	-1.30	—
February ..	0.39	1.80	-1.41	—
March ..	2.96	1.47	—	+1.49
April ..	1.94	1.61	—	+0.33
May ..	0.79	1.75	-0.96	—
June ..	4.15	2.10	—	+2.05
July ..	0.16	2.49	-2.33	—
August ..	3.27	2.38	—	+0.89
September ..	1.29	2.39	-1.10	—
October ..	1.40	2.76	-1.36	—
	17.13	20.83	-8.46	+4.76

Our bacteriological examinations of 262 samples taken during the month have given the results recorded in the following table. Besides these samples we have examined 453 others from special wells, standpipes, &c., making a total of 715 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 17 samples) ..	66
New River, filtered (mean of 51 samples) ..	3
Thames, unfiltered (mean of 18 samples) ..	35,177
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 140 samples) ..	16
Ditto ditto ..	highest 310
Ditto ditto ..	lowest 0
River Lea, unfiltered (mean of 18 samples) ..	87
River Lea, from the East London District clear-water wells (mean of 18 samples) ..	16

Of the 209 daily samples taken from the general filter wells of the Metropolitan Water Board, twenty-four samples, or 11.4 per cent, were sterile. Five samples, or 2.3 per cent, contained more than 100 microbes, and of these three samples contained more than 150 microbes per c.c. The five excess samples contained an average of 225 microbes per c.c. In September the one excess sample contained 110 microbes per c.c.

One very exceptional circumstance we have to record during the past month, and that is the extraordinary microbic condition of the River Thames. Between the 12th and the 18th the microbes rose from 320 to over a quarter of a million per c.c., and then as rapidly declined.

During the past ten months we have examined 10,712 samples of water bacteriologically, as compared with 9146, 8822, 6953, and 6893, respectively in the four previous years. We have also made 2312 chemical analyses of London waters during this period, making a total of 13,024 samples examined during the first ten months of this year.

Table B gives the bacteriological results for the past ten months. During the first six months the Thames-derived Districts' clear-water wells contained on an average 21 bacteria per c.c., while the New River, Lea, and Kent supplies contained 11, 22, and 9 respectively. During the past four months the numbers of bacteria from the same four sources were 21, 10, 18, and 10 respectively.

Table D gives the average chemical composition of the Thames-derived supplies during the year 1905. It will be observed that the amount of organic matter has been very low during the whole of this period, and exceptionally so during the past three months.

In presenting our final report, we take the opportunity of stating that we commenced the systematic examination of the London water in the autumn of 1880, and so have completed twenty-five years of continuous supervision of the chemistry and bacteriology of the Metropolitan Water Supply. During this period we have made chemical

TABLE B.—Showing the Average Monthly Bacterial Variations during the Year 1905.

Month.	Thames, unfiltered.	Thames- derived supplies, filtered.	New River, unfiltered.	New River, filtered.	River Lea, unfiltered.	River Lea (East London District), filtered.	Keot District, unfiltered.
January	4300	29	381	15	164	13	13
February	1392	13	220	8	174	27	30
March	8078	6	152	3	105	3	9
April	4887	19	106	13	175	27	3
May	1056	24	147	16	205	23	2
June	4493	38	206	16	264	41	1
	4034	21	202	11	181	22	9
July	6287	34	306	14	335	21	2
August	2535	21	146	18	330	28	23
September	2341	10	102	6	157	7	5
October	35177	16	66	3	87	16	—
	11584	20	155	10	227	18	10
	7809	20	178	10	204	20	9

Mean of 1st 6 months.

Mean of next 4 months.

Mean of 10 months.

TABLE C.—Average Number of Microbes in the Filtered London Waters for the Past Nine Years.

	Thames-derived supplies.	New River.	River Lea.
1897	46	32	62
1898	34	30	25
1899	27	15	20
1900	21	9	10
1901	24	10	22
1902	27	13	25
1903	36	16	26
1904	20	10	14
1905 (10 months)	20	10	20

TABLE D.—Averages of the Supplies derived from the River Thames during the Year 1905.

	Common salt per gallon.	Nitric acid per gallon.	Hardness. Degrees.	Oxygen required per gallon.	Organic carbon per gallon.	Organic carbon per gallon.	Colour. Brown: Blue.
	Means.	Means.	Means.	Means.	Means.	Maxima.	Means.
January	2 319	1'069	16'14	0'035	0'109	0'167	15'9 : 20
February	2 268	1'076	16'06	0'027	0'095	0'128	13 5 : 20
March	2 255	0 951	15'02	0'032	0'112	0'186	13 1 : 20
April	2'232	0 818	15'16	0'041	0'142	0'206	16 1 : 20
May	2'101	0 853	13'97	0'032	0'097	0'115	14 0 : 20
June	2 079	0 725	13 18	0'044	0'132	0 201	15 7 : 20
July	2'111	0'656	13'10	0'046	0'117	0 161	18'3 : 20
August	2'235	0'599	12'95	0'036	0'037	0'125	16'1 : 20
September	2'181	0'547	12 92	0'030	0'081	0 104	13'7 : 20
October	2'278	0'719	13'07	0'028	0'087	0'102	12'5 : 20

analyses of 58,489 samples and bacteriological examinations of 61,081 samples, making a total of 119,570 samples.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, November 2nd, 1905.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

MESSRS. W. B. Tuck, J. W. White, and E. W. Bealey were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Adam Lawson Kelly Adam, 296, Bath Street, Glasgow; C. Chester Ahlum, Lansdale, Pennsylvania, U.S.A.; James Edward Alcock, 42, Gill Street, Moston

Lane, Blackley; James Albert Allison, Luchana Laboratory, Apartado, 45, Bilbao, Spain; George Henry Barbrook, Stowmarket, Suffolk; Marmaduke Barrowcliff, 25, Priory Road, Kew, Surrey; John Coggin Brown, B.Sc., Fairleigh, Cockton Hill, Bishop Auckland; Joseph Edward Coates, B.Sc., Sunny Side, Oakmoor, Stoke-on-Trent; Douglas Henry Bellars Cowman, Heathville Corner, Gloucester; Arthur Augustine Dallman, Lyndhurst, Prospect Vale, Liverpool; John Llewelyn Davies, B.A., 8, Rugby Road, Neath; John Doull, 8, Lauriston Place, Edinburgh; John Beaconsfield Gall, Knoxland, Erith Road, Belvedere, Kent; Sidney Montague Haig, St. Edmund's Avenue, Port Hill, Stoke-on-Trent; Alfred Hart, M.A., B.Sc., Norman Avenue, Hawksburn, Victoria, N.S.W.; Jack Vernon Johnson Hayman, Tringhurst, Cranleigh, Surrey; John Michael Higgins, 39, Queen Street, Melbourne, Australia; William Basil Hill, Eastfield, Stockton Lane, York; Isaac Berkwood Hobsbaum, 79, Claremont Road, Forest Gate, E; Cecil Hollins, 34, Beamsley Road, Frizinghall, Yorks.; Maurice Brooks Jack, 66, Burma Road, Clissold Park, N.; Edward Towyn Jones, B.Sc., 17, Bloomsbury Square, W.C.; Rudolph Lyon, 400, Huddersfield Road, Halifax; William McCleary, 61, Station Road, Pendlebury, Manchester; Robert Drysdale MacKechnie, c/o Messrs. A. Boake, Roberts, and Co.,

Ltd., Stratford, E.; Harry Martin, 14, Hardman Street, Liverpool; Harry George Fletcher Micklewright, B.A., 116, St. James's Road, Croydon; Edalji Manekji Modi, opposite Grant Road Station, Bombay; John Motion, Edgewater, New Jersey, U.S.A.; Henry Allen Dugdale Neville, B.Sc., 81, Revidge Road, Blackburn; Francis Richard Penn, Highborne Terrace, Shadwell Lane, Moortown, Leeds; Hugh Donald Perkins, Dodwell, Bursledon, Hants; Percy Barker Phipson, c/o J. Staples and Co., Ltd., Wellington, N.Z.; Frederick John Pooler, B.Sc., The Boys' High School, Grahamstown, Cape Colony, South Africa; James Frederick Fothergill Rowland, B.A., 5, St. James's Park, Croydon; Harold Marmion Royle, 12, Barfield Villas, George Lane, S. Woodford; Harry Nestor-Schnurmann, Corinth House, Cheltenham; Douglas Temple Satterington, 45, Regent Road, Blackpool; John Booty Tillott, 55, Wood Street, Westminster, S.W.; Frank Tutin, 49, The Avenue, Kew, Surrey; George Stanley Walpole, 349, Queen's Road, Battersea Park, S.W.; John Ledger White, D.Sc., 73, Cambridge Mansions, Battersea Park, S.W.; Gerard William Williams, B.A., P.O. Box, 21, Germiston, Transvaal, South Africa.

The PRESIDENT referred to the loss sustained by the Society in the death of Professor P. T. Cleve, who was elected an Honorary and Foreign Member in February, 1883, and who died on June 18th, 1905; also in the death of Mr. G. B. Buckton, F.R.S., who was elected a Fellow in March, 1852.

Of the following papers, those marked * were read:—

*177. "Molecular Conductivity of Water." By PHILIP BLACKMAN.

The molecular conductivity of water may be represented by K and calculated from the equation—

$$\mu_{\text{HX}} + \mu_{\text{M}_1\text{OH}} - \mu_{\text{M}_1\text{X}} = K.$$

The value of K is dependent on (1) temperature, (2) molecular concentration, and (3) nature of the acid (μ_{HX} , $\mu_{\text{M}_1\text{OH}}$, $\mu_{\text{M}_1\text{X}}$ represent respectively the molecular conductivities, measured at the same temperature and molecular concentration, ν , of the acid HX, the base M_1OH , and the salt M_1X).

The conclusion is drawn that the greater the value of K the stronger is the acid, taking into consideration (1) the temperature and (2) the molecular concentration. This furnishes a method for determining the relative strengths of acids.

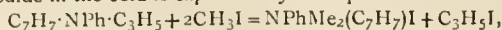
*178. "The Stereoisomerism of Substituted Ammonium Compounds." By HUMPHRY OWEN JONES.

The existence of Wedekind's isomeric α - and β -phenylbenzylmethylallylammonium iodides is so difficult to reconcile with the absence of isomerism in all the other compounds of the same type, that the author has examined these compounds in the hope of obtaining some information about this unique example of isomerism, and has found that the two compounds are not isomerides, but different compounds.

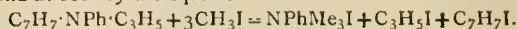
The β -compound dissociates partially into benzyl iodide and tertiary amine in chloroform solution, but is not transformed into the α -compound; it is also completely converted into phenyltrimethylammonium iodide when heated at 100° with methyl iodide in molecular proportions, whereas the α -compound requires twice as much methyl iodide to convert it into phenyltrimethylammonium iodide and benzyl and allyl iodides. Analysis and a comparison of properties prove conclusively that the β -compound is phenylbenzylidimethylammonium iodide.

The analyses of the compound previously given by Wedekind and by Hantzsch and Horn are incorrect, and the reactions described by the last-named chemists can only have been obtained with impure material.

The reaction between benzylallylaniline and methyl iodide in the cold is expressed by the equation—



and at 100° by the equation—



At present optical activity is the only evidence of stereoisomerism of quivalent nitrogen compounds of the type NabcdX , and, since the search for isomerides has been so thorough, it is concluded that no isomerides can be produced by the union of tertiary amines and alkyl iodides.

The hypothesis suggested by the author (*Trans.*, 1903, lxxxiii., 1403) to account for the non-formation of isomeric quivalent nitrogen derivatives from tervalent compounds is now adequate to explain all the known facts, and has been further developed.

DISCUSSION.

Mr. A. W. HARVEY stated that he had prepared considerable quantities of benzylphenylmethylallylammonium iodide, and that when the compound is produced by mixing molecular quantities of carefully purified benzylmethyl-aniline and allyl iodide in an equal volume of mixed methyl and ethyl alcohols (1—9) no trace of Wedekind's β -compound is formed; the reaction goes quite quantitatively, and yields a clean and pure solid product.

Dr. JONES, in reply, said that the β -compound was not produced together with the α -salt when allyl and benzyl iodides were added to the corresponding tertiary amines, but only when methyl iodide was used.

In reply to a question by Dr. Lapworth, the author stated that the evidence for the replacement of allyl by methyl in benzylallylaniline by the action of methyl iodide in the cold was quite conclusive, the benzyl group being only removed on heating.

*179. "Note on the Fluorides of Selenium and Tellurium." By EDMUND BRYDGES RUDHALL PRIDEAUX.

The fluorides of selenium and tellurium are both gaseous substances prepared by the action of fluorine on the elements, their densities corresponding to the formulæ SeF_6 and TeF_6 respectively. They are easily condensable by cold alone, forming white snow-like solids, the vapour pressure curves of which will be published shortly along with an account of the other properties of the gases.

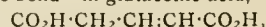
DISCUSSION.

Mr. BLISS asked whether the author could give any further information as to the nature of the solid fluorides isolated by Moissan.

Mr. PRIDEAUX, in reply, said that the solid fluoride of tellurium left in the reaction tube may be the tetrafluoride, TeF_4 , described as being obtained by the action of hydrogen fluoride on tellurous acid, but is more probably an oxyfluoride.

*180. "The Constitution of Glutaconic Acid." By JOCELYN FIELD THORPE.

The "double bond" in glutaconic acid,—



is apparently not fixed, since the reactions of this substance clearly indicate that it possesses a symmetrical structure.

Thus $\alpha\beta$ -dimethylglutaconic and $\beta\gamma$ -dimethylglutaconic acids, prepared by methods which leave no doubt as to their constitution, are not isomeric but identical. α -Methyl- β -ethylglutaconic acid and β -methyl- γ -ethylglutaconic acid are also identical.

Derivatives of glutaconic acid are produced when ethyl cyanoacetate or its monoalkyl derivatives react with ethyl acetoacetate or its monoalkyl derivatives, the ethyl salts formed yielding either (1) derivatives of glutaconic acid or (2) derivatives of 2:6-dioxypyridine, according to the nature of the hydrolysing agent and the constitution of the salt.

*181. "Some Alkyl Derivatives of Glutaconic Acid and of 2:6-Dioxypyridine." By HAROLD ROGERSON and JOCELYN FIELD THORPE.

Methods for the preparation of all the methyl derivatives of glutaconic acid are described, as well as the modes of preparation and properties of the corresponding derivatives of 2:6-dioxypyridine.

*182. "Note on the Formation of β -Methylglutaconic Acid and of α 3-Dimethylglutaconic Acid." By FRANCIS VERNON DARBISHIRE and JOCELYN FIELD THORPE.

By the elimination of hydrogen bromide from ethyl α -bromo- β -methylglutarate a mixture is obtained from which β -methylglutaconic acid can be isolated, the residue consisting of the lactone ethyl salt and the corresponding acid of the trimethylene ring.

From ethyl α -bromo- α 3-dimethylglutarate, similar products are formed, only in this case a much larger quantity of the glutaconic acid (α 3-dimethylglutaconic acid) can be obtained.

*183. "The Influence of Water and Alcohols on the Boiling-point of Esters. I. A Modification of Markownikoff's Method of Preparation." By JOHN WADE.

Ethyl acetate forms binary and ternary mixtures of minimum boiling-point with ethyl alcohol and water. The ternary mixture, which contains 9 per cent of alcohol and 8 per cent of water, boils constantly at 70.3° , whilst the binary mixtures, which contain respectively 8.6 per cent of water and 30.6 per cent of alcohol, boil constantly at 70.5° and 71.8° . Most esters form such mixtures with their constituent alcohols and water, and in preparing esters from acids and alcohols by Markownikoff's method of continuous distillation in presence of sulphuric acid (*Ber.*, 1873, vi., 1177), ternary mixtures are therefore usually obtained.

As the Markownikoff interaction, unlike the etherification process on which it is based, now proves on investigation to proceed in most cases readily at 100° , and in presence of any strong acid, it may be modified to afford a general and practical automatic method of preparing these ternary mixtures and their constituent esters in quantity. The lower alkyl esters of formic, acetic, propionic, and butyric acids have been made in this way under ordinary pressure, and various less volatile esters at the same temperature under somewhat reduced pressure. Owing to the peculiar relation of the binary to the ternary mixtures the excess of alcohol may often be removed from these products by distillation with water and fractionation.

*184. "Note on Bromine Fluoride." By EDMUND BRIDGES RUDHALL PRIDEAUX.

Fluorine when passed over bromine combines with it, as stated by Moissan, who has described the appearance of the reaction ("Le Fluor et Ses Composés"). The product, which is more unstable than iodine fluoride and decomposes water with great violence, has not been described. It is a pale yellow liquid with a specific gravity less than that of bromine, and freezes to a white solid which melts at -2° . The analysis of this fluoride leads to the formula BrF_3 , and this compound appears to be the only definite fluoride of bromine.

185. "Solution and Pseudo-solution." (Part IV.). By ERNEST LINDER and HAROLD PICTON.

The authors have completed, so far as they are able, the study of solution and pseudo-solution originated by them in 1892 (*Trans.*, lxi., 114–148). The results are arranged in three sections.

I. *The Physical and Chemical Properties of Colloidal Arsenious Sulphide.*—The precipitates, which separate when arsenious sulphide is coagulated by metallic salts, are regarded as metallic derivatives of a complex hydro-sulphide formed by interchange of hydrogen for metal. Thus, $x\text{As}_2\text{S}_3 \cdot \text{H}_2\text{S} + \text{BaCl}_2 = x\text{As}_2\text{S}_3 \cdot \text{BaS} + 2\text{HCl}$.

The coagulation process for salts of uni-, bi-, and trivalent metals is reviewed in the light of this hypothesis. Quadrivalent metals, such as platinum and zirconium, are found to be non-coagulants of arsenious sulphide in dilute solution.

The aggregation and de-aggregation phenomena of arsenious sulphide have been studied microscopically.

II. *The Physical and Chemical Properties of Colloidal Ferric Hydroxide.*—Various "grades" of colloidal ferric hydroxide have been prepared by dialysis. The physical

and chemical properties of certain of these solutions and the coagulation phenomena of the colloidal hydroxychloride have been studied by methods similar to those applied in the investigation on arsenious sulphide.

111. *Dyeing, a Phase of Coagulation.*—The "substantive dyeing" of colloidal ferric hydroxide and arsenious sulphide by methyl-violet and aniline-blue is shown to exhibit phenomena which are precisely analogous to those occurring when these colloids are coagulated by metallic salts.

186. "The Influence of very Strong Electromagnetic Fields on the Spark Spectra of Ruthenium, Rhodium, and Palladium." By JOHN EDWARD PURVIS.

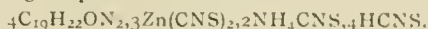
The experiments were made with a 21-foot concave grating spectroscope. The spark passed between electrodes of the metals which were firmly held between the poles of a magnet. The strength of the field between the poles of the magnet was 40,000 units with a current of 21 amperes. The nature of the vibrations was analysed by a calcite prism. The general results showed that (1) most of the lines are divided into triplets, and that there is a periodic or rhythmic change in the directions of the vibrations of the constituents of the triplets. (2) Some lines become quadruplets, and within certain definite regions of the spectrum their constituents also change the directions of their vibrations. (3) Other lines become doublets. (Only a very few lines are not affected when vibrating in the magnetic field). (4) The inner member of the triplets is usually the strongest; but this is not always the case. The two outer members of a triplet may be stronger than the inner one; and all three are sometimes equally strong. (5) The strongest spectral lines are not the most widely separated when vibrating in the field. Weak lines are usually more widely separated than strong ones. (6) The decrease in the width of the triplets does not proceed *pari passu* from the less refrangible to the more refrangible end of the spectrum.

187. "A Volumetric Method of Estimating the Cinchona Alkaloids by means of their Double Thiocyanates." By PHILIP WILFRED ROBERTSON.

Skey has pointed out that many alkaloids give precipitates with ammonium thiocyanate in the presence of a zinc or mercury salt. Many other metals act in a similar manner; zinc, however, forms the most insoluble precipitates. The alkaloids most sensitive to this reaction are quinine and the cinchona alkaloids. Thus in the presence of excess of zinc sulphate and ammonium thiocyanate, one part of quinine gives a distinct turbidity in 50,000 parts of water.

These precipitates prove to be double salts of considerable complexity, as is the case with the compounds of many alkaloids, more especially quinine and its allies.

Thus cinchonine ammonium zinc thiocyanate has the following composition:—



This formula corresponds closely with that of herapatite or iodoquinine sulphate,—



Notwithstanding the complexity of these double salts, the determination of the amount of thiocyanate removed from solution by the alkaloids forms an accurate and speedy volumetric method of estimating quinine in the commercial drugs and in the assay of the crude cinchona bark.

188. "The Osmotic Pressure of Sugar Solutions in Mixtures of Alcohol and Water." By PERCIVAL SMITH BARLOW.

Some experiments have been made with copper ferrocyanide membranes and solutions of sugar in a mixed solvent of alcohol and water, which confirmed Tammann's observation that an osmotic current cannot be obtained with these membranes and alcohol. The author's experiments were spread over a considerable time, in some cases months being allowed to elapse, so that every opportunity

might be afforded for the pressure to show itself. For membranes permeable to water only, the van't Hoff value of the osmotic pressure is very much diminished by the presence of the alcohol, but no idea has been obtained as yet of any relation between the amounts of alcohol present and the amount of the reduction in the pressures; below a certain strength of sugar solution there is no direct evidence of osmotic pressure, the alcohol present quite overshadowing the effect of the sugar. There are indications that the membrane is rendered permeable to the sugar by the presence of alcohol. For a membrane permeable to the alcohol only, the pressure set up is very much less than above, and is produced extremely slowly. Whatever molecular aggregates are formed in connection with the sugar, it seems that the alcohol molecule takes much less part in them than the water molecules.

Research Fund.

A Meeting of the Research Fund Committee will be held in December next. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on or before Monday, December 11th, 1905.

PHYSICAL SOCIETY.

Ordinary Meeting, November 24th, 1905.

Prof. J. H. POYNTING, F.R.S., President, in the Chair.

A PAPER on "*The Dielectric Strength of Air*" was read by Mr. A. RUSSELL.

The dielectric strength of air, at a given barometric pressure, is generally deduced from the results of experiments made on the disruptive voltages between equal metal electrodes at given distances apart. It is assumed that the electric field surrounding the two electrodes just before the disruptive discharge takes place is similar to that round the electrodes at low voltages. Schuster has shown that this assumption is untenable. The author has found that in certain cases the dielectric has broken down before the final discharge takes place. Hence the boundaries of the Faraday tubes are no longer the surfaces of the metal electrodes, but the boundary of that part of the dielectric surrounding the two electrodes which has ceased to insulate and has become a conductor. It is known that for various gases there are certain minimum sparking potential-differences between the electrodes. The electrostatic equations fail to take this into account. The author therefore makes the assumption that for distances apart greater than about a millimetre when the disruptive voltage is V kilovolts the effective P.D. between the ends of the Faraday tube which is subject to the maximum stress is $V - \epsilon$, where ϵ is the minimum sparking voltage. Applying formulæ which he has deduced, using this assumption, to tests of Heydweiller, Steinmetz, Algermissen, &c., the author finds that they agree in making the dielectric strength of air 38 kilovolts per c.m. approximately. A knowledge of this quantity enables us to find not only the disruptive voltages between electrodes of many geometrical shapes, but it also enables us to find the "critical" pressure for overhead electric-power transmission at high pressures. The author gives a complete proof by Kelvin's method of images of the Kirchhoff series-formula, and shows how its numerical value can be readily found both by ordinary algebra and by elliptic function series.

Dr. H. A. WILSON expressed his interest in the author's explanation of the brush discharge and the formation of coronas. There were, however, one or two points in the paper which required some alteration. The author stated that according to Strutt the minimum sparking potential-difference was 767 volts when the barometric pressure was 72.4 c.m. The pressure in Strutt's experiments was, however, 72.4 m.m. When the distance between the electrodes was not too small it was known that the sparking P.D. could be expressed as $V = a + \beta d$, where d

was the distance between the electrodes and a and β were constants. This constant β the author had called the dielectric strength of air, but he did not think he was justified in doing so.

The CHAIRMAN, referring to Table V. in the paper, asked if the rise in value of the dielectric strength as the distance apart of the electrodes increased was due to the formation of coronas.

Mr. RUSSELL, in reply, thanked Dr. Wilson for pointing out that in the paper the atmospheric pressures at which Mr. Strutt had obtained his results were quoted in c.m. instead of m.m. Mr. Strutt had shown that the P.D. between the cathode and the negative glow was 341 volts whatever the atmospheric pressure. We were therefore quite justified in assuming that at ordinary pressures the electric pressure on the Faraday tube subject to the maximum stress is $V - \epsilon$, where ϵ is greater than 341. The experimental results analysed in the paper indicate that ϵ is 0.8 of a kilovolt. In answer to Prof. Poynting, he stated that the slight rise in the values of the dielectric strength in Table V. was probably due to the potentials of the electrodes not being V and zero at the instant of discharge.

A paper by Dr. H. A. WILSON and Mr. E. GOLD, "*On the Electrical Conductivity of Flames for Rapidly Alternating Currents*," was read by Dr. WILSON.

This paper contains an account of a series of experiments on the electrical conductivity of a Bunsen flame containing various alkali-salt vapours for alternating currents with frequencies from 7×10^4 to 11×10^5 alternations per second. The conductivity was measured between two platinum electrodes immersed in the flame, and the variation of the conductivity with the amount of salt present and with the nature of the salt was investigated. The variation of the conductivity with the frequency of alternation, the maximum E.M.F., and the distance between the electrodes was also examined. The results obtained enable a comparison to be made between the conductivities of various alkali-salt vapours for alternating currents and their conductivities for steady currents as previously determined. The conductivity was measured by means of a Wheatstone's Bridge, three arms of which consisted of small air-condensers and the fourth of the electrodes in the flame. One of the condensers could be adjusted until a balance was obtained. The following is a summary of the results:—1. For rapidly alternating currents a flame containing an alkali-salt vapour behaves like an insulating medium of high specific inductive capacity. 2. The conductivity of different alkali-salt vapours in a flame for rapidly alternating current as measured by the apparent capacity of platinum electrodes immersed in the flame, varies as the square root of the conductivity of the same salt vapours for steady currents. This result confirms the view that the negative ions from all salts have the same velocity. 3. The apparent capacity varies nearly inversely as the square root of the maximum applied P.D. 4. The apparent capacity is nearly independent of the number of alternations per second. 5. The apparent capacity is nearly independent of the distance between the electrodes. 6. The results 1 to 5 are in agreement with the ionic theory of the conductivity of the flame for rapidly alternating currents when the velocity of the positive ions and the inertia and viscous resistance to the motion of the negative ions are neglected in comparison with the effects due to the number of ions per c.c. 7. The apparent capacity per sq. c.m. area of the electrodes is equal to $\frac{4\pi e}{8\pi V_0}$, where n is the number of positive ions per c.c., e the charge on one ion, and V_0 the maximum applied P.D. 8. Not more than molecule in ten of salt molecules is ionised at any instant, but each molecule is probably ionised and re-combines several million times per second. 9. The steady currents observed through salt vapours in flames are very far from the maximum possible currents corresponding to the number of ions produced per second.

Mr. W. DUDELL expressed his interest in the method of measurement and referred to the fact that although the paper was entitled "The Electrical Conductivity of

Flames," the Authors had not measured conductivities, but a complex quantity which was equivalent to a resistance shunted with a condenser. He drew attention to one of the tables given in the paper in which numbers referred to as constant varied by over 50 per cent.

Dr. WILSON said the quantity which they had measured was the apparent capacity of the electrodes.

A paper "On the Lateral Vibrations of Loaded and Unloaded Bars" was read by Mr. J. MORROW.

This is a continuation of the work previously communicated by the author on the "Vibration of Bars of Uniform and Varying Sectional Area." By means of a method of continuous approximation, the elastic displacement curves and the frequency of the lateral vibrations of bars can be determined to any required degree of accuracy. The method is first applied to some cases of unloaded bars, and also to massless bars carrying concentrated loads. The paper then deals with the principal problems of loaded bars which are themselves of appreciable mass. The equations in their general forms are cumbersome, but for a given position of the concentrated load and for a given ratio of the mass of the load to that of the bar the expressions for the frequency become very simple. In order to reduce the results to a form available for practical use, the numerical constants in these expressions have been worked out for the different positions of the load and for ratios of mass of load to that of bar ranging from 0 to 1.0. In the last section of the paper the method is applied to find the corrections due to the rotatory inertia of the masses and of the sections of the bar, and a comparison is given with the methods employed by Lord Rayleigh and Dr. Chree for similar purposes.

CORRESPONDENCE

ESTIMATING THE CONSTITUENTS OF DOLOMITE.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS, September 8th, 1905 (vol. xcii., p. 108) Mr. Nicholas Knight criticises the method of estimating the constituents of dolomite, as described in our text-book on Quantitative Analysis.

The method there described is not intended for the use of industrial analysts, but is given as an example for students who are commencing the analysis of minerals. It is therefore a typical analysis, and as such we deem it should be exact.

As some of the estimations are described for the first time in this analysis, and are subsequently frequently referred to, precautions are suggested which would be unnecessary in a commercial analysis of a limestone.

Below are appended reasons why these methods are chosen.

1. *Silica*.—In siliceous limestones an appreciable quantity of silica goes into solution when the substance is dissolved in hydrochloric acid, hence in accurate analysis it is necessary to evaporate to dryness and heat the residue to 150° C.

2. *Iron Oxide and Alumina*.—If small quantities of ferric and aluminium hydroxides are precipitated in the presence of much calcium salt, we have found that the first precipitation with AmOH always carries down some calcium.

In the analysis given below, in which the ordinary laboratory reagents were used, 0.09 per cent of lime was found to be thus co-precipitated. In order to make sure that its precipitation was not due to the ammonium hydrate having been slightly carbonated, some freshly prepared ammonia solution was made by passing ammonia gas into recently boiled distilled water. This reagent was used to precipitate the hydroxides of iron and aluminium, and the precipitate was filtered and washed. It was then dissolved in hydrochloric acid, precipitated again with the fresh am-

monia solution, and filtered off. The filtrate was found to give a distinct precipitate with ammonium oxalate solution, showing that calcium had been originally precipitated with the ferric and aluminium hydroxides.

3. *Magnesia*. If great care is taken that ammonium salts are present in small quantity only, it is not absolutely necessary to ignite before precipitating the magnesium as double phosphate. But since students frequently add ammonium salts freely, and in the method suggested by us powdered ammonium oxalate is added to ensure the rapid formation of a granular precipitate, it is necessary to ignite before estimating the magnesium.

In an estimation carried out under the above conditions 14.62 per cent of MgO was found after ignition, but only 14.44 was found if the ignition was omitted.

Recent analyses of a dolomite made in one of our laboratories serve to indicate the different results obtained by the method suggested by us (A) and that by Mr. Nicholas Knight (B).

	Method A.	Method B.
Fe ₂ O ₃ + Al ₂ O ₃	1.35	1.43
CaO	37.04	37.03
Additional CaO brought down with		
Al ₂ O ₃ and Fe ₂ O ₃	0.09	—
MgO	14.62	14.58

The CaO in Method A was obtained after a single precipitation of the ferric and aluminium hydroxides by ammonia solution.

It will be seen that after a second precipitation of these oxides a further quantity of calcium was obtained from the filtrate. This amount almost exactly makes good the difference in the percentages of Fe₂O₃ + Al₂O₃ obtained by the two methods.

The difference in the percentages of MgO is not so important.—We are, &c.,

FRANK CLOWES.
J. B. COLEMAN.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

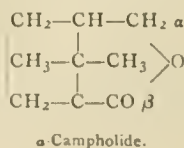
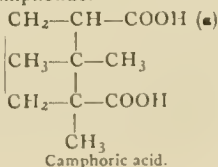
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

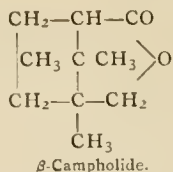
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 18, October 30, 1905.

This number contains no chemical matter.

No. 19, November 6, 1905.

On the Mixed Function Derivatives of Dextro-camphoric Acid, and on the β -Campholide.—A. Haller and G. Blanc.—In a previous communication, one of the authors showed that camphoric anhydride reduced in alcohol by sodium amalgam generates a lactone, α -campholide, reproduced later by MM. Baeyer and Williger by treating camphor with potassium sulphate and sulphuric acid, and quite recently by reduction of the α -methyl acid camphorate. This lactone can be converted into nitrile by potassium cyanide, then into homo-camphoric acid, the lead salt of which, on calcining, gives camphor, with its original properties. These reactions show that it is easy to pass from camphoric acid to camphor. But in camphoric acid the bonds of union of the two carboxyl groups are not identical, so that it is possible to imagine a second campholide, which they call β -campholide.



 β -Campholide.

This compound, treated in the same way as the α -campholide, should give a nitrile, a homocamphoric acid, and, finally, a new camphor isomeric with the corresponding derivatives of the α -compound. Unsuccessful attempts to prepare this δ -lactone had already been made in 1866. The authors then experimented with β -methyl acid camphorate, which is formed by saponification of neutral methyl camphorate with alcoholic potash. They then reduced it with sodium and absolute alcohol, following a method which resulted in the transformation of isolauroic acid into the corresponding alcohol. After the preparation of the

β -chloride, $\text{C}_8\text{H}_{14} \left\langle \begin{array}{c} \text{CO}_2\text{CH}_3 \\ \text{COCl} \end{array} \right\rangle \alpha$, the authors passed readily to the methyl- β -camphoramate, the β -phenylhydrazine of the α -methyl compound, and propose to return later to the preparation of many mixed derivatives of camphoric acid from this chloride. From the α -chloride, $\text{C}_8\text{H}_{14} \left\langle \begin{array}{c} \text{COCl} \\ \text{CO}_2\text{CH}_3 \end{array} \right\rangle \beta$

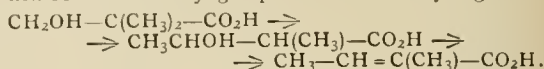
they prepared the β -methyl- α -camphoramate, crystallising in more beautiful crystals than its isomer above, but possessing a smaller rotatory power. The anilide, p -toluide, and phenylhydrazide ethers could not be obtained in crystalline form. The β -campholide was prepared by reducing a solution of 50 grms. of β -methyl acid camphorate in 350 grms. of alcohol by 50 grms. of sodium. The campholide was extracted with ether and purified by crystallisation. A kilogram. of β -acid ether only gave 26 grms. of lactone. The β -campholide crystallises in a mixture of ether and petroleum ether, the crystals melting at $218-220^\circ$ in a closed tube. It is very soluble in alcohol and ether in hot soda, but is re-precipitated by mineral acids. The authors tried to pass this β -campholide through the same changes as the α -compound, in order to interchange the CO and CH_2 groups, but with little success. They arrive at the following conclusions:—

1. That it is possible to obtain β -campholide isomeric with that prepared by one of them from the reduction of camphoric anhydride, but that this new lactone does not easily lend itself to double decomposition with potassium cyanide.
2. That the α - and β -camphoric acid ethers (ortho and allo) supply corresponding ether chlorides capable of giving molecules of mixed function. Even if they have not succeeded in attaining their end, the authors maintain that their researches bring into prominence the great functional differences shown by certain groupings according to the molecule to which they are attached. In the β -campholide, as in the β -camphoric acid ethers, the functional groups which resist the action of reagents are both united to the

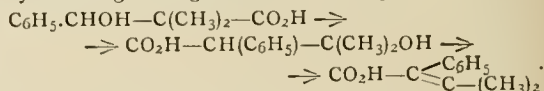
carbon $\begin{array}{c} | \\ \text{—C—} \\ | \\ \text{CH}_3 \end{array}$, whilst in their α -isomers the same groupings are attached to the carbon $\begin{array}{c} | \\ \text{—C—} \\ | \\ \text{H} \end{array}$. It seems that the presence of one atom of hydrogen united to the carbon which is attached to the group CO_2R or $\text{CH}_2\text{>O}$ favours a reaction.

Molecular Transpositions and Migration of the Carboxyl Group in the Dehydration of certain Hydroxy Acids.—E. E. Blaise and A. Courtot.—It is well known that δ -hydroxy acids dehydrate easily, giving non-saturated β -acids. But when the α -carbon is dialcoylated this mode of dehydration is no longer possible up to the present. Acting with phosphoric anhydride on the ethers of the dimethylhydracrylic acids, the authors have obtained ethers of non-saturated β -acids. Particularly they have prepared dimethylvinylacetic acid, the constitu-

tion of which they previously established. The same method gave dimethylpropenylacetic, dimethylisopropenylacetic, and dimethylphenylvinylacetic acids, of which more anon. From the point of view of dehydration, the most interesting of the ethers are those not possessing any hydrogen united to the γ -carbon, or those in which—the alcoholic function being primary—the chain is limited to the β -carbon. The authors find that, on dehydrating oxypivalic acid, a hemipolylactide is obtained; but by acting on the ethylic ether the dehydration is accompanied by a transposition, and a mixture of tiglate and angelate of ethyl is obtained. The reaction necessitates a permutation between a methyl-group and an atom of hydrogen.—



The formation of dimethylatropic acid by the dehydration of dimethylphenylhydracrylic acid can only be explained by admitting the migration of the carboxyl,—



This interesting reaction, so far as the authors are aware, is the first observed example of the migration of the carboxyl group in a synthetical molecule. It shows that this migration may be normal in certain transformations on natural substances, as, for instance, the conversion of camphoric acid into isolauroic acid.

MISCELLANEOUS.

Messrs. F. Wiggins and Sons, Mica Merchants, announce that their only address now is 102/103, Minories, London, E.C.

MEETINGS FOR THE WEEK.

- MONDAY, 4th.—Society of Arts, 8. (Cantor Lectures). "Measurement of High Frequency Currents and Electric Waves," by Dr J. A. Fleming, F.R.S.
- Society of Chemical Industry, 8. "Notes on Gutta-percha and Balata," by W. A. Caspari. "Determination of Zinc in Zinc-aluminium Alloys," by R. Seligman and F. J. Willott. "Distilled Water Supply for Works Laboratories," by R. Seligman. "Estimation of Naphthalene in Coal gas," by C. J. Dickinson-Gair. "Salts of the Alkaloid Cinchonamine," by B. F. Howard and F. Perry.
- Royal Institution, 5. General Monthly Meeting.
- WEDNESDAY, 6th.—Society of Arts, 8. "The Manufacture of Sugar from British grown Beet," by Sigmund Stein.
- Society of Public Analysts, 8.
- THURSDAY, 7th.—Society of Arts, 4.30. "The Partition of Bengal," by Sir James A. Baurdillon.
- Chemical, 8.30. "The Constitution of Nitriles—Part I., Two varieties of Silver Nitrite," by P. C. Ray and A. C. Ganguli. "The Products of Heating Silver Nitrite," by E. Diversa. "Ethyl Piperonyl Acetate," by W. H. Perkin, jun., and R. Robinson. "Contribution to the Chemistry of Saccharin," by F. D. Chattaway. "Action of Heat on α -Hydrocarboxylic Acids" (Part II.), by H. R. Le Sueur. "Studies on Optically Active Carbimides—Part II., The Reaction between 1-Methylcarbimide and Alcohols," by R. H. Pickard, W. O. Littlebury, and A. Neville. "Action of Ultra-violet Light on Moist and Dried Mixtures of Carbon Monoxide and Oxygen," by S. Chadwick, J. E. Ramsbottom, and D. L. Chapman.

GOVERNMENT GRANT to defray the expenses of Scientific Investigations. Applications for the year 1906 must be received at the Offices of the Royal Society not later than JANUARY 31st next, and must be made upon printed forms to be obtained from the Clerk to the Government Grant Committee, Royal Society, Burlington House, London, W.

THE CHEMICAL NEWS.

VOL. XCII., No. 2402.

NEW RESEARCHES ON THE ATOMIC WEIGHT OF NITROGEN.*

By PHILIPPE A. GUYE

In different ways, which, however, agree in their results, the conclusion is to-day arrived at that the atomic weight of nitrogen, as found by Stas, is inaccurate. The error is 1/467 if one refers to the value $N = 14.04$ of the International Table for 1905; it is 1/311 if one takes the number assigned (1882) by the illustrious Belgian chemist, $N = 14.055$. In other words, the probable value of the atomic weight of nitrogen is $N = 14.01$.

In the first place it may be asked how, since the celebrated work of Stas, published in 1860 and 1865, chemists have been able to content themselves with a value containing so considerable an error without its having been discovered; it seems particularly strange that the numberless nitrogen estimations carried on yearly in the different departments in which this element plays so important a part—such as it plays in inorganic or organic chemistry, in rural economy, in the explosives industry, &c.—have not served to make the error apparent. I see only one plausible explanation; it is that the great majority of chemists have continued to make their calculations with the round number $N = 14.00$, adopted about 1843, as a result of Marignac's work, this number differing from the correct number by 1/1400.

However that may be, it is evidently not possible to abandon the results of an experimenter so eminent as Stas without being absolutely sure that they are erroneous. This explains and justifies the wisdom of the International Committee on Atomic Weights, which certainly cannot be reproached for having so far retained the value $N = 14.04$. But to-day, in spite of the great and legitimate admiration which the labours of Stas everywhere inspire and will long continue to inspire—and I am of the number of his admirers, of those in particular who cherish a remembrance of the kind reception of the Master in his laboratory in Brussels—the moment has come in which one should have the courage to break with the past and to recognise the error committed. The careful examination of the question, the substance of the review of research upon the subject, demonstrate:—

1. That the classical gravimetric methods pursued by Stas, by his predecessors, or by his successors, are not capable of sufficient accuracy to guarantee the second decimal of the atomic weight of nitrogen.
2. That the new methods of a physico-chemical nature allow, on the other hand, of attaining to this accuracy, and point to the value $N = 14.01$.
3. That the new gravimetric methods, more rational and more accurate than those previously followed, lead to results which confirm the value of the atomic weight of nitrogen obtained by the physico-chemical methods.

It is these three classes of considerations that I desire now to investigate with you.

But, to begin with, it is desirable to say a few words on the history of the question. It was first in 1895 that serious doubt was cast by Lord Rayleigh and Sir William Ramsay upon the atomic weight of nitrogen. Having determined with great accuracy the density of chemical nitrogen, these scientists estimated this density, referred to that of oxygen ($O = 16$), to be 14.003; for atmospheric

nitrogen, mixed with argon, this ratio is 14.07, coinciding nearly with Stas's number, 14.055 or 14.06, a singular fact but not unique in the history of science, which has certainly contributed towards giving a false confidence in the accuracy of this number.

Shortly afterwards M. Leduc, at the conclusion of his beautiful researches upon gases, was led in 1897 to substitute for the value $N = 14.075$, which he had proposed in 1894 for the atomic weight of nitrogen, the number $N = 14.005$.

It is this same value $N = 14.005$ that D. Berthelot finally arrived at in his remarkable memoir on the method of density-limits (1898), based principally on the observations of MM. Leduc and Sacerdote.

Finally, in 1900, in the course of researches on the constants of the equation of Van der Waals, which have obliged us to choose as exact a value as possible for the atomic weight of nitrogen, Friderich and I adopted the number $N = 14.005$, relying principally on the ratio of the densities of nitrogen and hydrogen, corrected to the mean of the compressibility experiments by Regnault.

While these physico-chemical experiments were being carried on, certain revisions by gravimetric methods were undertaken, but without leading to any conclusive results. This at least is the impression gained by reading reviews by Richards, a scientist particularly competent to judge of these matters, and from whom I borrow the following summary:—

TABLE I.—Methods.

	N.
Ratio—HCl : NH_3 (Thomsen, 1894)	14.021
Ratio—Ag : $AgNO_3$ (Hardin, 1896)	14.01
Ratios— $\left\{ \begin{array}{l} KNO_3 : KCl \\ NaNO_3 : NaCl \end{array} \right\}$ (Hibbs, 1896) ..	14.01
Ratio—AgCN : Ag (Dean, 1900)	14.031
Analysis—Salts of nitrous acid (Ramsay and Aston, 1903)	13.903
Ratio— $Na_2CO_3 : 2Na_2NO_3$ (Richards)	14.02
Ratios— $\left\{ \begin{array}{l} CsNO_3 : CsO_2 \\ KNO_3 : KO_2 \end{array} \right\}$ (Richards & Archibald, 1904)	14.037 to 14.040

The latest experiments of Richards and Archibald in particular were not of the nature to dissipate the discordance between the physico-chemical results, on the one hand, and the gravimetric results on the other; this in effect was a confirmation of the international atomic weight $N = 14.04$.

In the presence of such a want of agreement, the more profound study of the question imposed itself afresh: either the classic methods or the physico-chemical are in error; one of the contradictory results should be discarded.

With the view to endeavour to elucidate this problem, various researches of an experimental or theoretic nature were undertaken in my laboratory, from the years 1901 to 1902, the object of the one being to determine different points connected with the physico-chemical methods, the others to lay the foundation of new gravimetric methods more rational than those employed hitherto.

The work entailed by the execution of the programme thus traced was considerable; it would not have been possible to bring it to a satisfactory conclusion in so short a time without the valuable and enlightened co-operation of friends and former pupils; my assistant, Dr. A. Jaquero, as well as Drs. St. Bogdan, C. Davila, L. Demolis, E. Mallet, L. Perrot, A. Pintza, and O. Schener, have kindly assisted in the different sections of these researches.

It is therefore of the sum of this work that I shall speak, and it is from the discussion of their results, a discussion frequently general, that the three fundamental conclusions I just now formulated have arisen.

I am thus brought back to my subject; it only remains for me to ask your indulgence for the use of numerical tables which I am obliged to lay before you in order to make clear to you the conviction gained after a personal effort of many years.

(To be continued).

* From the *Bulletin de la Société Chimique de Paris*, 1905.

SOME OBSERVATIONS ON COLUMBIUM.*

By ROY D. HALL and EDGAR F. SMITH.

(Continued from p. 254).

Reactions of the Double Fluorides of Columbium, Titanium, Tantalum, Tin, and Tungsten with various Reagents in Concentrated Sulphuric Acid.

A SMALL amount of the reagent was dissolved in eight to ten drops of concentrated sulphuric acid on a glazed porcelain surface, and the crystalline double fluoride introduced into this acid solution. In most cases the colour was destroyed upon diluting with water. No colour was imparted to tin solutions by any of the reagents which appear in the accompanying table.

Reagent.	Ta.	Cb.	Ti.	W.
Codeine ..	No colour.	No colour.	Faint pink, may be due to morphine.	Light brown; on standing, trace purple.
Morphine ..	Faint yellow.	—	Red to brown, very delicate.	Grey - brown, becoming purple; H ₂ O ppt.
Resorcinol ..	No colour.	No colour.	Red-brown, fairly delicate.	No colour.
Naphthol (β) ..	"	Faint yellow brown.	Coffee brown, very delicate.	Brown, becoming dark blue.
Naphthol (α) ..	"	Faint brown.	Green to dark greenish brown.	Deep blue, very delicate.
Pyrogallol ..	"	Yellow to light brown.	Dull dark red.	Deep red to brown to dirty blue.
Salicylic acid ..	"	Very faint yellow.	Deep red.	Reddish yellow.
Cinchonidine ..	"	No colour.	No colour.	On standing, a slight purple.
Apomorphia ..	"	Yellow brown.	Light red-brown.	Purple to brown to green and blue.
Narceine ..	"	Brownish yellow.	Brown.	Dirty dark green.
Bebeerina ..	"	No colour.	Clear brown.	Dark brown to green.
Narcotina ..	"	Yellow.	Brown.	Light brown to green.

Strychnia, quinidia, cinchonidine, and atropia gave no colour with any of the elements tested. Narceine and bebeerina alone in sulphuric acid gave a considerable colour, and with them the amount of reagent must be very small, or it will obscure any change produced by the addition of the double fluoride. In this connection it is of interest to note that Levy (*Comptes Rendus*, ciii., 1074, 1195) studied the colours produced by the phenol-like bodies, dissolved in concentrated sulphuric acid, when brought in contact with the oxides of titanium, tin, tantalum, columbium, and other elements, with the following results:—Columbium could be tested for in the presence of all the others by using codeine, as it gave a pink colour, while titanium yielded no colour, and tantalum but a faint green. Titanium could be tested for by using morphine, with which it gave a carmine colour, columbium no colour, and tantalum a yellow colour passing into brown. Tantalum with resorcinol gave a dirty green colour, changing to amethyst and rose, while titanium yielded a flesh-red colour, going to chocolate-brown, and columbium a yellowish tint. None of the results were duplicated save the morphine test for titanium, which proved exceedingly delicate: yet to have the colour show definitely in columbium the latter must contain 0.5 per cent of TiO₂. Codeine gave no colour with columbium, nor did resorcinol with tantalum, therefore Levy could not have had pure material for his tests.

In our use of these reagents we failed to find satisfactory tests, except in the case of morphine for titanium. None answered for columbium in the presence of titanium, or for tantalum in the presence of columbium. Resorcinol proved to be a fairly delicate test for titanium; it gave no colour with columbium, tantalum, or tungsten.

Action of Hydrochloric Acid Gas on Ignited Columbic Oxide.

0.25 gram. of ignited columbic oxide was completely volatilised in three hours in a current of dry hydrochloric

acid gas. It volatilised as a white powder, with no indication of reduction by change of colour. The compound formed adhered to the walls of the glass tube, was insoluble in oxalic acid, and only very slowly soluble in concentrated sulphuric acid, requiring long boiling to dissolve a thin layer. It contained hydrochloric acid, as was shown by washing with ammonium hydroxide and testing the washings with silver nitrate and nitric acid. It would be very difficult to collect in a form convenient for analysis; yet this should be done, as the body evidently contains no water, as is given in the formula of a similar body obtained by Smith and Maas (*Zeit. Anorg. Chem.*, vii., 96) by passing moist hydrochloric acid gas over the hydrated oxide. It is undoubtedly analogous to the body obtained on heating molybdic acid in hydrochloric acid gas, namely, MoO₃.2HCl. It is probably Cb₂O₅.xHCl.

Action of Sulphuric Acid on the Hydrates of Columbium and Titanium after Precipitation by Ammonium Hydroxide from Solutions of their Double Fluorides.

The method used was to precipitate the hydrates from a weighed amount of the double fluorides, filter, and wash as thoroughly as possible; then transfer to a weighed platinum dish, re-weigh (the difference being water), after which a weighed amount of sulphuric acid of definite specific gravity was added and allowed to stand in contact with the hydrates for a definite time. The portion insoluble was filtered off, and the amount of oxide going into solution determined by precipitation with ammonium hydroxide, igniting, and weighing. The amount of titanium in the oxide which went into solution was determined colorimetrically.

In making these trials columbium oxyfluoride was used in which the titanium oxide, as compared with the columbium oxide, was 0.00095 gram. TiO₂, or 0.41 per cent. The specific gravity of the sulphuric acid used was 1.145.

Experiments.

1. One gram. of K₂TiF₆, containing 0.3330 gram. of TiO₂, was used to obtain the hydrate. The latter was treated with 40 c.c. of water and 70 grms. of sulphuric acid. I dissolved completely in fifteen minutes.

2. 0.4450 gram. of columbic oxide, in the form of hydrate was treated with 40 grms. of water and 108 grms. of sulphuric acid for one hour. Only a slight precipitate was obtained with ammonium hydroxide in the filtrate. It was not weighed, but contained 0.00032 gram. of TiO₂, or 0.07 per cent of the total oxide taken, or one-sixth of the total TiO₂ present.

3. Columbic hydrate, containing 0.4450 gram. of oxide, was treated with 60 grms. of water and 123 grms. of sulphuric acid for four hours. The portion which dissolved equalled 0.0060 gram. = 1.33 per cent, and contained 0.000424 gram. of TiO₂, or 7 per cent of the oxide dissolved, and about one-fourth of the total titanium present.

4. The hydrate from 3 grms. of columbium oxyfluoride, equivalent to 1.35 grms. of oxide, was allowed to stand in

* *Proceedings of the American Philosophical Society*, 1905, xlv., p. 177.

contact with 50 grms. of water and 100 grms. of sulphuric acid for seventeen hours. The acid solution showed 0.0236 grm. of oxide = 1.75 per cent, containing 0.000954 grm. TiO_2 = 4 per cent of oxide dissolved, or 17 per cent of the total TiO_2 present.

5. Hydrate containing 0.445 grm. of oxide, when treated with 57 grms. of water and 85 grms. of H_2SO_4 (specific gravity = 1.435) for forty-five hours, showed in solution 0.0500 grm. = 11.1 per cent, containing 0.0008 grm. TiO_2 = 1.6 per cent of the oxide dissolved, or 43 per cent of the total TiO_2 present.

Known amounts of the two hydrates were next treated together as in the following experiments:—

6. 0.2816 grm. of K_2TiF_6 , containing 0.0939 grm. of TiO_2 , and 0.5078 grm. of $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, containing 0.2255 grm. C_2O_3 , were treated with 50 grms. of water and 15 grms. of sulphuric acid (specific gravity = 1.435) for four hours. The amount of oxide remaining insoluble was only 0.07 grm. It was not examined as to its titanium content.

7. The hydrate from 0.2420 grm. K_2TiF_6 , containing 0.0807 grm. TiO_2 , and that from 0.3454 grm. of $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, containing 0.1537 grm. of C_2O_3 , were covered with 70 grms. of water and 5 grms. of sulphuric acid of specific gravity 1.435. The amount of oxide in solution after four hours was 0.0800 grm., corresponding well with the weight of the oxide of titanium present, but the insoluble portion was found to contain 0.0350 grm. of TiO_2 , determined colorimetrically; so that only about one-half of the titanium hydrate had been dissolved out, while nearly as much columbium hydrate had gone into solution. The acid used would not have dissolved any columbium hydrate had it been free from titanium hydrate; further, it would have dissolved out all of the titanium hydrate had it not been mixed with the columbium hydrate. It may therefore be concluded that this method of separation is worthless. It remains to be seen how haloid acids would act.

The Chromotropic Acid Test for Titanium.

Geisow (Dissertation, 1902) observed that the colour developed by chromotropic acid with titanium solutions offered a very delicate test for that element. In concentrated solution it gives a deep red, in dilute solutions a pink colour. The colour-giving compound was isolated by Geisow, and found to have the following composition:—One molecule of chromotropic acid to four of TiO_2 and nine of H_2O .

As it was most important to find some means of estimating the amount of titanium in columbium we were induced to study this reaction of Geisow, using solutions of titanic hydrate in oxalic, sulphuric, and hydrochloric acids.

Solutions Used.

- A. 0.53 grm. of TiO_2 dissolved in 3.42 grms. of oxalic acid and diluted to 500 c.c. 1 c.c. = 0.00106 grm. of TiO_2 , and contained 0.00684 grm. of oxalic acid.
- B. Ten c.c. of A diluted to 100 c.c. 1 c.c. = 0.000106 TiO_2 .
- C. Ten c.c. of B diluted to 100 c.c. 1 c.c. = 0.0000106 TiO_2 .
- D. Ten grms. of oxalic acid in 100 c.c. 1 c.c. = 0.1 grm. of oxalic acid.
- E. One grm. of chromotropic acid in 100 c.c.

50 c.c. Nessler tubes, 1 inch in diameter, were used for all of the tests.

0.5 c.c. of E in 50 c.c. of water gave a mere trace of colour, for which reason the solution to be tested was always compared with another tube containing the same amount of chromotropic acid, thus making allowance for the slight colour given by the solution of that reagent.

0.15 c.c. of C gave a faint pink colour when added to 50 c.c. of water containing 0.5 c.c. of E; 0.00000159 grm. of TiO_2 in 50 c.c. of water gave a change of colour; 0.3 c.c. of the same solution gave a very distinct colouration, or 0.00000318 grm. of TiO_2 in 50 c.c. More than 1 c.c. of the chromotropic acid gave so much colour as to interfere with the delicacy of the test.

(To be continued).

PHYSICAL SOCIETY.

EXHIBITION OF ELECTRICAL, OPTICAL, AND OTHER PHYSICAL APPARATUS.

THIS Exhibition will be held at the Royal College of Science, South Kensington, on Friday Evening next, December 15th, from 7 to 10 p.m.

Invitations have been issued to Members of the Institution of Electrical Engineers, the Röntgen Society, the Optical Society, and the Faraday Society.

Admission will be by ticket only.

The following is a brief description of the exhibits:—

MESSRS. R. AND J. BECK, LTD.

Spherometer so arranged that the measuring-point is held up against the surface of the lens by a uniform counter balance pressure. This counter balance is pivotted slightly to one side of the central plunger in such a manner that the measurement of the plunger is enormously magnified at the setting line. It is also arranged so that all the strains are practically along one central line. The measurements are read upon a barrel which is graduated to read to 0.00001 inch.

Proof Glasses showing Interference Method of Testing Optical Surfaces.—Proof glasses showing flat and curved surfaces, also approximately flat surfaces with proof glasses upon them showing various defects.

Photographic Lens Testing Bench.—Designed for rapidly detecting and measuring the various aberrations of photographic lenses. Suitable for the swinging test for taking the curvature of field and astigmatism of photographic lenses, and at the same time giving their equivalent focus. Also for practically all the known methods of lens testing, including those introduced by Prof. Hartmann of Potsdam.

Diffraction Grating Direct Spectroscope.—Containing a Thorp diffraction grating cast from a Rowland grating, and placed upon a prism in such a manner that the emergence is practically direct with the incidence. The dispersion is about equal to a train of five flint prisms.

Pocket Direct-vision Diffraction Spectroscope.—A small instrument with a large dispersion obtained by a diffraction grating; having also a travelling indicator reflected in the field of view in such a manner that it can be travelled to any portion of the spectrum. Its position is read upon a graduated milled head, so that the spectrum can be divided into about 500 parts.

Microscope specially designed for Metallurgical Work.—The distance between the nose-piece and stage is particularly large, and the object can be easily focussed without interfering with the illuminating apparatus.

Microscope for Petrological Work.—Embodying the principle invented by Mr. A. B. Wick. Other features are the special adjustment of the analyser, method of rapidly removing the top lens of the condenser system, and a particularly large vulcanite-covered stage.

THE CAMBRIDGE SCIENTIFIC INSTRUMENT CO.

Einhoven String Galvanometer, with arc lamp, as designed by Prof. W. Einhoven and modified by Mr. W. Duddell. The moving conductor is a silvered quartz-fibre stretched with adjustable tension in the field of a very powerful electromagnet, and imaged with a magnification of about 500 on a transparent scale. The movement can also be examined visually by means of a microscope.

Duddell Thermo-galvanometer.—An instrument for the measurement of very small direct or alternating current. It has practically no self induction, and can be used on a circuit of any frequency even up to 120,000 per second, and currents as small as 20 microamperes can be readily measured by it. The uses of the instrument are very many and very obvious; amongst other uses it can be used to measure the currents in the receiving aerial in Wireless Telegraphy.

Duddell Twisted Strip Ammeter.—A very sensitive instrument for measuring direct or alternating current. The mechanical period is very short, so that it is able to follow currents which vary over a small range as rapidly as one or two cycles per second. This instrument is most useful for observing the quick variations of the R.M.S. voltage in supply stations produced either by cyclic irregularity of the engine or by phase-swinging between alternators, converters, &c.

Broca Galvanometer, as designed by Prof. A. Broca and modified by Dr. Harker, of the National Physical Laboratory. The suspended system consists of a pair of needles whose axis is vertical, one being so magnetised as to have a north-pointing pole in the middle, while the other is magnetised inversely. A high figure of merit is attained, and the coils are readily exchanged for others of different resistance.

Dolezalek Electrometer.—The needle is suspended by a quartz-fibre which is rendered conductive by being dipped in a calcium-chloride solution and connected to any convenient source of E.M.F.; or the needle is charged and insulated, the fibre being left dry.

Grassot Fluxmeter, with large permanent magnet for demonstration, and **Duddell Magnetic Standard**. A ballistic instrument whose suspended coil has a large moment of inertia, and in which the torsional control is appreciable, so that the retarding couple acting on the coil is proportional to its angular velocity, the magnetic field in which the coil lies being of sensibly uniform intensity. When an electromotive impulse is applied to it the coil is deflected, and comes definitely to rest in a new position, the deflection being proportional to the electromotive impulse, and independent of its time-distribution.

Cadmium Cell, H Form.—E.M.F. 1.1095 volts at 18° C.; mean temperature coefficient 0.000025 volt per centigrade degree rise. To the specification of the National Physical Laboratory.

Bridge for teaching Resistance Thermometry, with thermometer in glass tubes, and D'Arsonval Galvanometer simple form. An inexpensive outfit for teaching.

New Form Recording Thermo-couple, with Thermo-couple fitted with reels of spare wire in head attached to Recorder. The galvanometer-boom carries a knife-edge, which is intermittently depressed upon an inked thread, one point of which is thus brought into contact with a drum. The ordinate of the point in question is measured lengthwise of the thread, the co-ordinates of the record being rectangular.

Melloni Bench, for observing the reflection, refraction, absorption, &c., of radiant energy.

Spectrometer.—The construction is especially rigid, and the collimation axis cannot be displaced by the adjustment of the eye-piece focus.

Telescope and Scale.

Astronomical Micrometer for determining micrometrically the co-ordinates of stars upon a celestial photograph impressed with a standard réseau.

Trouton Hygrometer.—A continuous recording hygrometer designed by Prof. F. T. Trouton, F.R.S., and depending on the varying weight of flannel or other fabric when in equilibrium with air of varying humidity.

Vertical Sonometer.—Two wires can be directly loaded by weights, and the vibrating length of one can be varied and clamped without the introduction of a frictional error in the estimated load.

Perry's Apparatus for Teaching Law of Helical Springs, similar to that described in Prof. Perry's "Applied Mechanics."

Burton Levelling Stand.—A geometric gimbal construction provides for two independent levelling motions about mutually perpendicular axes, the adjustments being perfectly free and without side-shake. Either adjustment can be altered while the other is clamped.

Stands for holding apparatus, with universal clamps, and Time Markers (Deprez and simple double marker).

MESSRS. CROMPTON AND CO.

Electrometer, devised by Mr. W. A. Price, M.A., in which the fixed and moving members are parts of concentric spheres. The pivot is at the common centre of the spheres, and the air-gap between the fixed and moving parts is unchanged by deflection or swinging.

Electrical Pyrometer, of the thermo-electric type, for engineering measurements. The thermo-couple is of nickel and steel. The steel element is in the form of a tube down the centre of which runs an insulated nickel rod. This form of couple is used for temperatures up to 1100° C.; for a lower range of temperatures the couple is of copper and constantan. The scale of the instrument at the cool junction takes account of the temperatures of the two junctions and of the average temperature of the whole apparatus.

Set of Laboratory Standard Resistances wound with manganin and aged. The cases may be filled with petroleum when inverted, and fitted with thermometers.

MESSRS. ELLIOTT BROTHERS.

Electrical Measuring Instruments.

MESSRS. EVERETT, EDGCUMBE, AND CO.

Portable Photometer, designed for low price, and for rapid testing with fair accuracy without any special precautions being taken as to exclusion of stray light, regulation of voltage, &c.

Watt-photometer—a higher class portable instrument than the last-mentioned—containing a wattmeter in the photometer case, and so arranged that the efficiency in watts per c.p. is read off on the instrument scale.

Standard Photometer, direct reading, designed for laboratory use. Includes arrangement for testing arc lamps at different angles. Errors from stray light, inequality in the two sides of the photometer, &c., are compensated for as far as possible. A combined Flicker and Trotter head is employed, so that either method may be used at will.

Ammeters and Wattmeters for taking rapid measurements of power consumed by glow-lamps.

Frequency Indicator, consisting of a number of steel tongues with different periods of vibration. These are acted upon by an electro-magnet energised by the current whose frequency is desired, and the vibration is taken up by the tongue having a period corresponding with the frequency.

MR. PETER HEELE.

Large Spectrograph fitted with optical parts made of ultra-violet glass.

Spectrograph—a smaller pattern.

Solar Spectroscope, Evershed pattern.

Large Direct-vision Spectroscope, of new design.

MESSRS. A. HILGER.

Spectroscope.—Measuring in wave-lengths direct. It is calibrated on over 200 spectrum lines, and reads accurately to within 1 Angström unit from wave-length 3883 to wave-length 7724. The length of scale on a spiral drum is about 60 inches. The instrument is of the constant deviation type.

Standard Goniometer.—Prism table reads to 30 seconds and the telescope to 1 second of arc. Fitted with reflecting prisms, so that the circle can be read by the microscope without the observer moving away from the telescope.

MARCONI'S WIRELESS TELEGRAPH CO.

Cymometer, designed by Dr. J. A. Fleming, F.R.S., for making exact measurements of wave-lengths and frequencies in wireless telegraphy, or in similar high-frequency circuits. The instrument can also be used to determine small capacities, or the inductance, within certain limits, of a high-frequency circuit.

(Demonstrations will be given with this instrument).

MESSRS. NALDER BROS. AND THOMPSON.

Portable Standard Testing Set (with ohmmeter and generator).—The special feature of this set is the electrostatic instrument.

MESSRS. NEWTON AND Co. (in the Library).

Projecting Lanterns for projecting both apparatus and slides. These are triple, rotating, with three fronts which can be fitted at will with attachments for showing slides; transparent apparatus, opaque apparatus and specimens, microscopic and polariscope objects, spectrum apparatus, &c., and by swinging the lantern round any required front can be brought into play at a moment's notice. The "Transpaque" lantern is a simple and inexpensive form of projection apparatus, which in a few minutes can be altered for direct, vertical, or opaque projection, as well as for low microscopic powers, &c.

Polariscopic and Microscopic Preparations.

Induction-Coil and other X-Ray Apparatus.—The set of X-Ray and High Frequency apparatus as shown comprises all that is needed for a hospital or private experimenter.

(Demonstrations will be given at intervals).

Mr. R. W. PAUL.

Universal Pyrometers and a small electric Muffle Furnace.

Duddell-Mather Standard Wattmeters and gauze resistances.

Reflecting Galvanometer, vibrationless, with new pattern scale and Nerst lamp.

Galvanometers, of the single pivot portable type.

Electrostatic Voltmeters (reflecting) for low readings.

Paul Harris Portable Test-wire.

Potentiometer Outfit, with accessories.

Standard Resistances for laboratory work.

Nerst-Paul Lamps and Lanterns for demonstration purposes.

(The Pyrometers will be shown in action).

MESSRS. JAMES PITKIN AND Co.

Holden D'Arsonval Galvanometer.—A very sensitive instrument having two suspension strips, practically unaffected by vibration. Intended to withstand rough usage.

Electric Pyrometers.—Various forms, portable and otherwise, for use in factories.

Resistance Boxes, Standard Cells, galvanometer keys and scale stands.

Measuring Instruments — ammeters, voltmeters, recorders, and cell testers.

MESSRS. RUMNEY AND RUMNEY.

Bastian Mercury Vapour-Lamps.—Illumination of the Library by means of these lamps.

(Demonstrations will be given at intervals).

MESSRS. CARL ZEISS.

An Optical Appliance to facilitate Visual Perception of Ultra Microscopic Particles.—The apparatus consists of a projection table provided with an arc lamp, optical bench, two projection aplanats, and a precision slit. The image of the source of light is projected on to the precision slit by means of one of the aplanats; the second aplanat then serves for the purpose of projecting an image of the slit, reduced to $\frac{1}{4}$ diameters, at a distance of about 90 m.m. from the lens. The microscope situated at the end of the optical bench, and fitted for the observation of fluids, with a water immersion objective and a special trough with quartz windows, is used upright, and the objects illuminated horizontally with a very narrow beam of light. An achromatic objective, mounted on a sole-plate with cross-slide, serves as a condenser. Either fluids or solid objects may be observed.

(Gold particles in colloidal solution will be shown with the apparatus. The particles are less in size than 10μ).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, November 16th, 1905.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

DR. JULIEN DRUGMAN was formally admitted a Fellow of the Society.

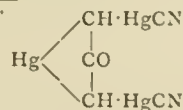
Certificates were read for the first time in favour of Messrs. William Edward Bell, 88, Monks Road, Lincoln; Thomas Harold Durrans, 1, Cornwall Terrace, Regent's Park, N.W.; Walter Hamis Glover, Ph.D., 38, Ribblesdale Road, Streatham, S.W.; William Prince Hayworth, 119, Clapton Common, London, N.E.; John Kirby Shrimpton, 22, Fountains Terrace, North Road, Ripon; Franklin Wilfred Walker, 39, Graham Road, Acton Green, W.; Richard Alfred Warren, Belle Vue, Hallow Road, Worcester; Harold Joseph Wheaton, 21, Chesterton Road, Cambridge; Herbert William Mills Willett, The Cedars, Chislehurst; Ernest Edwin Wolfe, Kinsale, Co. Cork, Ireland.

Certificates were authorised by the Council for presentation to ballot under By-law I. (3) in favour of Messrs. Charles Anthony, jun., Town Hall, East London, Cape Colony; John Dunlop Millen, Launceston, Tasmania; Henry Rowley, Perth, Western Australia.

Of the following papers, those marked * were read:—

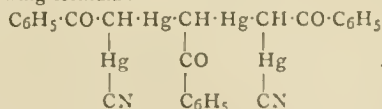
*189. "Condensation of Ketones with Mercury Cyanide." By JAMES ERNEST MARSH and ROBERT DE JERSEY FLEMING-STRUTHERS.

Acetone added to a solution of mercury cyanide in aqueous caustic soda gives a white precipitate, $\text{Hg}_3\text{C}_5\text{H}_7\text{ON}_2$, insoluble in water or alcohol, which dissolves on further addition of acetone. The best yield is obtained with one molecule of acetone to not less than fifteen molecules of mercury cyanide. No precipitate at all is formed with one molecule of acetone to less than two molecules of mercury cyanide. The reaction forms a good test for acetone applicable also in presence of alcohol. The following formula represents the probable constitution of the compound:—



The same substance is formed by adding acetone to a solution of mercury cyanide and sodium ethoxide in alcohol, or sodium methoxide in methyl alcohol. The compound, which is decomposed by hydrochloric acid with liberation of acetone and hydrogen cyanide, is also decomposed by aqueous potassium cyanide with liberation of acetone. Strong sulphuric acid attacks it slowly, forming a soluble compound which is being further investigated.

Acetophenone yields a similar compound, $\text{Hg}_3\text{C}_6\text{H}_5\text{O}_3\text{N}_2$, with mercury cyanide in aqueous caustic soda; the constitution of this product may probably be represented by the following formula:—



The reactions appear to be confined to ketones containing the group $\text{CO} \cdot \text{CH}_3$; precipitates were not obtained with diethyl ketone, benzophenone, menthone, or camphor. But ethyl acetacetate and diphenylmethyl ketone give similar compounds. Precipitates were also obtained with ethyl malonate and ethyl isosuccinate. Aldehydes generally bring about a reduction of the mercury cyanide. Benzaldehyde and anisaldehyde give almost quantitatively their respective acids.

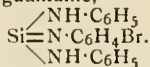
*190. "Silicon Researches. Part IX. Bromination of Silicophenylimide and -amide, and Formation of a Compound including the Group (SiN)." By JAMES EMERSON REYNOLDS.

In Part VII. of this series of papers, the author showed that the fine crystalline silicophenylamide, $\text{Si}(\text{NHC}_6\text{H}_5)_4$, described in Part V., can be made to afford silicotriphenylguanidine, and, ultimately, silicodiphenylimide, $\text{Si}(\text{NC}_6\text{H}_5)_2$. The latter is isomeric with the still unknown silicocyanamide, $\text{SiN}\cdot\text{N}(\text{C}_6\text{H}_5)_2$. The aim of the present inquiry has been to study the action of bromine directly on the di-imide, or indirectly through the silicophenylamide in the hope of forming a compound including the group SiN analogous to cyanogen.

The di-imide in the form of very fine powder was found to combine with two atomic proportions of bromine, even in the cold, when the halogen was present in benzene solution, the insoluble additive compound, $\text{Si}(\text{NC}_6\text{H}_5)_2\text{Br}_2$, being formed. When this substance was warmed with excess of bromine, also diluted with much benzene, the aniline residues were attacked and variable mixtures were obtained, which proved to be very difficult to separate. On the other hand, silicophenylamide, being easily soluble in benzene, was found to be much more suitable for the systematic study of the products of bromination.

One molecular proportion of silicotetraphenylamide in benzene solution interacts quite regularly with about six atomic proportions of bromine, also dissolved in benzene, provided the temperature is kept down and the addition of the halogen made very slowly. The colour of bromine disappears, and a precipitate forms from the outset consisting of aniline and bromoaniline hydrobromides. It was found, however, that three successive stages can be recognised in this interaction, and each one has been closely examined.

1. In the first stage, bromine (2 atoms) effects the removal of one of the aniline residues in the form of hydrobromide, which separates out, and there remains in solution the substituted guanidine,—



2. At the second stage, the guanidine is attacked by a similar proportion of bromine, which causes the removal of more hydrobromide and the formation of a soluble disubstituted di-imide, $\text{Si} \equiv \text{N}\cdot\text{C}_6\text{H}_4\text{Br}$. This substance does not appear to form another additive compound analogous to that afforded by the unsubstituted di-imide.

3. The third stage in which another molecule of bromine acts on the substituted di-imide, is to some extent conditioned by the dilution of the benzene solution in which the interaction takes place; but the chief change involves the removal of a third aniline residue, leaving in solution the SiN compound $\text{SiN}\cdot\text{C}_6\text{H}_3\text{Br}_2$.

Under varying conditions, more or less of at least one other substance is formed, with the elimination of HBr, namely, $\text{Si} \equiv \text{N}\cdot\text{C}_6\text{H}_4\text{Br}$ and, probably, a still smaller proportion of $\text{Si} \equiv \text{N}\cdot\text{C}_6\text{H}_3\text{Br}_2$.

The nitrile, when purified as far as is at present possible, is a dark coloured, vitreous solid, fusible at about 60° . It is easily decomposed by water and alcohol, but is dissolved as a whole by pure ether, provided the temperature is not allowed to rise above 5° . At the ordinary temperature, the solution decomposes, and ethyl silicates are formed, whilst a brown precipitate slowly separates, chiefly consisting of a bromoaniline derivative.

Treatment with excess of bromine leads to the production of silicon bromide and hydrogen bromide, whilst highly brominated anilines separate.

*191. "Application of the Microscopic Method of Molecular Weight Determination to Solvents of High Boiling-point." By GEORGE BARGER and ARTHUR JAMES EWINS.

The method by which the vapour pressures of two solutions are compared by measuring microscopically the change in thickness which drops of these solutions undergo when placed in a capillary tube, was originally worked out by one of the authors for use at the laboratory temperature (*Trans.*, 1904, lxxxv., 286). A hot stage is now described, which can readily be made, and by means of which the tubes can be kept under observation at a constant temperature (up to 95°). The capillaries are fastened to a microscope slide, which is fixed with a spring inside a glass tube, about 25 m.m. wide, through which a stream of hot water flows, thus keeping the temperature constant to within one or two degrees. This tube is provided with a thermometer, and rests in a block of wood on the microscope stage.

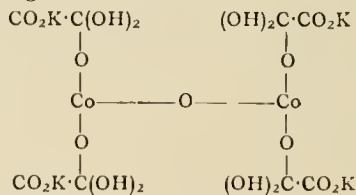
With volatile solvents, such as alcohol and benzene, 1 per cent differences in the molecular concentration of two solutions can be detected in five to ten minutes at a temperature of about 80° . With aniline, the least volatile solvent which can be conveniently employed, the corresponding time at 95° is one hour.

The solvent need not be pure; oil of turpentine, for example, gave satisfactory results. The time required for a complete determination is about an hour and a-half; for the mere verification of a probable formula, much less time is necessary. The average error in thirty determinations quoted is 3 per cent. Pyridine, acetic acid, and aniline are the best of the less volatile solvents examined.

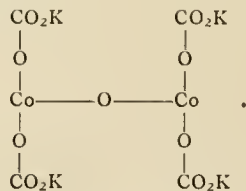
*192. "Green Compounds of Cobalt produced by Oxidising Agents." By REGINALD GRAHAM DURRANT.

Methods of obtaining green compounds by oxidising cobaltous salts in presence of the alkali salts of acetic, tartaric, citric, oxalic, lactic, malic, succinic, and glycolic acids were given. The preparation, analysis, and properties of green crystalline potassium cobaltic oxalate were set forth in detail, and evidence was adduced in support of the existence of analogous crystalline ammonium cobaltic and calcium cobaltic oxalates.

The conclusions arrived at are that (1) these substances most probably all contain the nucleus $\text{>Co}\cdot\text{O}\cdot\text{Co}<$, the oxalate being,—



and the carbonate—



2. The prevailing green colour in these cobaltic compounds with carboxylic salts depends on the persistence of the complex $\text{Co}\cdot\text{O}\cdot\text{Co}$.

3. The differences observable in the tints and in the absorption spectra of the various green solutions depend probably on the varied association of carboxyl groups attached to this nucleus.

*193. "Dunstan, Fowett, and Golding's Paper on the Rusting of Iron." By EDWARD DIVERS.

The fact which throws into the background all others contained in the important paper by Dunstan, Fowett, and Golding on the rusting of iron (*Trans.*, 1905, lxxxvii., 1548), and, indeed, constitutes its substance, is that even the purest available iron is freely rusted by oxygen and

liquid water, unaided by carbon dioxide or any other substance. Yet, in the construction of the paper, this fact seems to have been subordinated, perhaps without intention, to the setting forth of, and submitting evidence for, the theory that the rusting of iron is a process involving the formation of hydrogen peroxide. Accordingly, the publication (*Proc.*, 1903, xix., 150) of a preliminary abstract of the contents of the full paper led Moody (*loc. cit.*, p. 157) to suppose Dunstan's contention to be that ordinary rusting is caused by hydrogen peroxide. There is, therefore, reason to fear that those chemists who may hesitate to accept the hydrogen peroxide theory will be apt to overlook the fact that whether with or without the intervention of hydrogen peroxide, iron rusts when in contact with nothing more than an aqueous solution of oxygen.

Now the truth of the authors' theory to explain the fact may well be doubted, although they themselves hold that they have obtained a considerable body of experimental evidence in favour of the temporary formation of hydrogen peroxide. For, in support of the theory, no other fact is to be found in the paper than that the alkalis and other substances, which interfere with the existence of hydrogen peroxide, likewise prevent the rusting of iron. But the coincidence here observed is fully and accurately accounted for, without dependence on hydrogen peroxide, as being the result of the inability of oxygen and water in presence of one of these substances to act together as *hydroxyl*, whether it be to form hydrogen peroxide, $(HO)_2$, or such a compound as zinc hydroxide, $Zn(OH)_2$. Hydrogen peroxide is not wanted in order to explain the rusting of iron; indeed, its production stands rather in the way of a simple theory. What is wanted is the presentation of free or at least available hydroxyl groups to unite with the iron. Again, it is hardly a tenable argument that a substance, because it interferes with the existence of another substance, must likewise prevent its formation. For instance, ferrous sulphate ends the existence of free chlorine, but it does not prevent manganese dioxide and hydrochloric acid in contact with it producing the atomic chlorine, which it immediately proceeds to consume.

Moritz Traube explained and experimentally illustrated what he called the "autoxidation" of metals and other substances as being the chemical intervention of the water molecule between that of the autoxidising substance and that of the oxygen. Water, which cannot be acted on by either alone, is capable of chemical partition between the two; with zinc present to seize the hydroxyl of the water, the oxygen can take the rest of its hydrogen to form hydrogen peroxide, and, accordingly, this substance is not an uncommon product of autoxidation. It is easy and natural to admit that, with the great evolution of energy in the union of zinc with hydroxyl, only the small addition of energy afforded by the hydrogenation of free oxygen into hydrogen peroxide should be sufficient to half dehydrogenate the oxygen of water. Traube's equation satisfactorily represents therefore the formation of the hydrogen peroxide. The authors, however, give equations which are indistinguishable from those suggested by Hoppe-Seyler, although they very rightly reject this physiological chemist's conception of the nature of oxidation. They write (*loc. cit.*, p. 1549) $Fe + O_2 + H_2O = FeO + H_2O_2$ [Traube would have written it $Fe + 2OH \cdot H + O_2 = Fe(OH)_2 + H_2O_2$]. Again, on p. 1564, they write $Fe + OH_2 = FeO + H_2$; $H_2 + O_2 = H_2O_2$, equations which have none of the acceptability of Traube's. Can it be admitted that iron may do what potassium cannot do, displace all the hydrogen of water? Can it be allowed by the laws of thermal chemistry that cold water can be endothermically oxidised into hydrogen peroxide? There is another equation, given to explain the action of hydrogen peroxide on iron, to which also exception must be taken: $Fe + H_2O_2 = FeO + H_2O$. Surely if the equation holds good at all, the right side of it should be written $Fe(OH)_2$, the hydroxyls uniting with the iron, even if, afterwards, water separates.

The conversion of iron into rust seems to be as fully explained and as simply displayed as the facts allow by the

following equation: $(O_2 + 2H \cdot HO) + 4Fe + 2O_2 = 4HO \cdot Fe \cdot O$, or, if preferred, $2(HO)_2 \cdot Fe_2O_3$. If it is proper, as it apparently may be, to represent the ferrous and the ferric oxidation as distinct, then the above equation may be resolved into $(O_2 + 2H \cdot HO) + 4Fe + O_2 = 2(HO \cdot Fe'')_2O$ (ferrous oxyhydroxide) and $2(HOFe')_2O + O_2 = 4HO \cdot Fe'''O$. Putting these equations into words, rusting consists in the oxidation of iron by oxygen, with the intervention of water as hydroxyl hydride to the extent of two molecules for every three molecules of oxygen consumed. (Instead of the six molecules of water required by Traube's equation in the theoretical production of $Fe_2(OH)_6$.) To account for the non-formation of hydrogen peroxide nothing need be advanced; that seems to come as a matter of course. The point to be explained is, rather, the very production of this substance during the autoxidation of zinc and other substances. Why do not all the hydroxyls combine with the zinc, instead of a very small proportion of them remaining as hydrogen peroxide? The equation $Zn + 2OH \cdot H + O_2 + Zn = 2Zn(OH)_2$, seems to express accurately what really does happen to a very great extent.

DISCUSSION.

The following communication from Prof. DUNSTAN was read by the Secretary:—"In the preceding note, Dr. Divers has expressed the fear that the important fact established in the paper by Drs. Jowett and Goulding, and myself, that iron will rust in an aqueous solution of oxygen without carbon dioxide will be overlooked. This fear is, however, not justified in view of the explicit statements contained in the paper and the prominence given to the experimental evidence.

"Dr. Divers is of opinion that the intermediate formation of hydrogen peroxide, suggested as a working hypothesis to account for the observed facts, is unnecessary, but the alternative view expressed by him as 'the presentation of available or free hydroxyl groups to unite with iron' is not intelligible, unless it amounts to what is virtually the same hypothesis, which accounts for the inhibiting effect of potassium dichromate as well as of alkalis.

"With regard to the mechanism of the change, it has not been suggested, as Dr. Divers supposes, that water is oxidised by hydrogen peroxide. On the contrary, Traube's view of the formation of hydrogen peroxide is accepted. The outline equations in the paper (*Trans.*, 1905, lxxvii., 1548) were not intended to do more than represent the general nature of the change, and may equally well be written to show that the metal takes the hydroxyl and not strictly the oxygen of the water. There is no exception to be taken to the condensed equations Dr. Divers gives in conclusion, but unless the intermediate formation of hydrogen peroxide is assumed, they do not explain the inhibiting effect of alkalis or of other salts. There is no evidence to show that alkalis interfere with the formation of simple hydroxides such as $Zn(OH)_2$.

"Dr. Divers fails to offer any satisfactory explanation of the undoubted formation of hydrogen peroxide during the 'rusting' of zinc, where the process at work must be strictly analogous to that which occurs in the case of iron.

Mr. A. C. CHAPMAN said that it was rather surprising that investigators who had studied the rusting of iron and the action of water on other metals in the presence of oxygen should have apparently devoted so little attention to the influence of traces of metallic impurities in the metals under observation. Such charges were, of course, electrolytic in nature, and it seemed to him very probable that in many cases the action would be very greatly modified if metals of a very high degree of purity could be used in the experiments. Dr. Divers had referred to the combined action of oxygen and water on metallic zinc, and he had recently had occasion to observe how very greatly this was affected by the presence of very slight traces of nickel, cobalt, or other metallic impurities in the zinc employed.

In reply, Dr. DIVERS referred Prof. Dunstan and also

Dr. Jowett to his foregoing note, in which it is explained that the inhibitory action of such a substance as potassium hydroxide or dichromate is fully accounted for as being due to its making oxygen and water unable to behave either as hydroxyl towards iron or as hydroxyl for becoming hydrogen peroxide. He thought with Mr. Chapman that even the purest zinc yet used may have been active upon air and water through electrolysis by means of some impurity.

He was aware that the authors had treated iron as being acted on by hydrogen peroxide, but all that he had wished to contend against had been their assumption that air and water owe their activity to a production of hydrogen peroxide. Dr. Moody had fully shown that hydrogen peroxide in pure water is inactive upon iron.

*194. "Researches on the Freezing-points of Binary Mixtures of Organic Substances; the Behaviour of the Dihydric Phenols towards *p*-Toluidine, *α*-Naphthylamine, and Picric Acid." By JAMES CHARLES PHILIP and SYDNEY HERBERT SMITH.

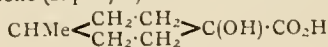
Investigation of the freezing-point curves demonstrates the existence of several new compounds of the above substances. As might have been expected, it was found that catechol and resorcinol were able in certain cases to form two compounds with a base; for example, catechol forms two compounds with *p*-toluidine containing the constituents in the molecular ratio of 1:1 and 1:2 respectively, and freezing at 50.4° and 41.5°. Since the 50 molecular per cent compound crystallises sluggishly, it is possible to realise metastable freezing-points on the adjacent branches of the curve. In this respect, the 50 per cent compound is similar to $\text{Fe}_2\text{Cl}_6 \cdot 7\text{H}_2\text{O}$ in Roozeboom's curve for the hydrates of Fe_2Cl_6 . Resorcinol and *p*-toluidine were also found to combine in two proportions.

Quinol does not form compounds so readily as resorcinol and catechol, and in the case of quinol and *α*-naphthylamine only a slight indication of the formation of a compound is obtained in the form of an intermediate branch of the curve which does not reach a summit.

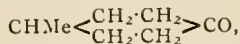
The picrates of catechol and resorcinol, as shown by the freezing-point curves, are well-defined compounds containing a molecule of each constituent. The freezing-point of catechol picrate is higher than the freezing-point of either component.

195. "Synthesis of Tertiary Menthol and of Inactive Menthe." By WILLIAM HENRY PERKIN, jun.

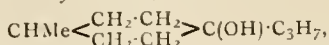
When hexahydro-*p*-toluic acid is treated with phosphorus pentachloride and bromine, it is converted into *α*-bromo-hexahydro-*p*-toluic acid (Perkin and Pickles, *Trans.*, 1905, lxxxvii., 645), which melts at 109—110°, and is hydrolysed by dilute sodium carbonate with formation of *α*-hydroxy-hexahydro-*p*-toluic acid (m. p. 132°), and Δ^1 -tetrahydro-*p*-toluic acid. The hydroxy-acid is readily decomposed by sulphuric acid with elimination of carbon monoxide, and the solution, on dilution with water, yields 1:4-methyl-cyclohexanone (b. p. 170°):—



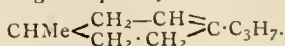
yields—



considerable quantities of Δ^1 -tetrahydro-*p*-toluic acid being produced at the same time. 1:4-Methylcyclohexanone reacts readily with magnesium isopropyl iodide, and is converted into tertiary menthol,—



which distils at 95° under 25 m.m. pressure (compare Baeyer, *Ber.*, 1893, xxvi., 2270), and when digested with potassium hydrogen sulphate yields inactive menthe.—

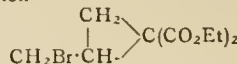


This synthetical hydrocarbon distilled at 168°, and

yielded the characteristic nitrosochloride melting at 128°; there can therefore be no doubt that it is the inactive modification of menthe (compare (Urban and Kremers, *Am. Chem. Journ.*, 1894, xvi., 395).

196. "The Synthetical Formation of Bridged Rings. Part II. Some Derivatives of Dicyclobutane." By WILLIAM HENRY PERKIN, jun., and JOHN LIONEL SIMONSEN.

When the sodium derivative of ethyl malonate (one molecule) is digested with tribromopropane, $\text{CH}_2\text{Br} \cdot \text{CHBr} \cdot \text{CH}_2\text{Br}$, an ester of the formula $\text{C}_{10}\text{H}_{15}\text{O}_4$ is obtained which distils at 154° (26 m.m.), and evidently has the constitution—



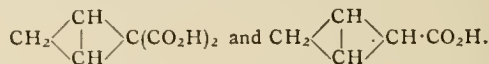
Alcoholic potash decomposes this ester with formation of a crystalline acid, $\text{C}_4\text{H}_4(\text{CO}_2\text{H})_2$, which melts at 139°, is only slowly oxidised by permanganate, and does not decolorise a solution of bromine in chloroform; it is not reduced when its solution in sodium carbonate is boiled with a large excess of sodium amalgam, and, when treated with hydrobromic acid, it is converted into a hydroxy-acid, $\text{C}_4\text{H}_5(\text{OH})(\text{CO}_2\text{H})_2$, which melts at 150°.

It is readily esterified by alcohol and sulphuric acid, yielding an ester, $\text{C}_4\text{H}_4(\text{CO}_2\text{Et})_2$, which distils at 129° (22 m.m.).

When the acid $\text{C}_4\text{H}_4(\text{CO}_2\text{H})_2$ is heated, it loses carbon dioxide with formation of the corresponding monobasic acid, $\text{C}_4\text{H}_5\text{CO}_2\text{H}$, which melts at 57°, and yields an ester, $\text{C}_4\text{H}_5\text{CO}_2\text{Et}$, which distils at 160—161° (765 m.m.).

The monobasic acid is not reduced when its alkaline solution is boiled with excess of sodium amalgam; it does not decolorise bromine, and when treated with hydrobromic acid or hydriodic acid it yields a dihydrobromide, $\text{C}_4\text{H}_7\text{Br}_2 \cdot \text{CO}_2\text{H}$ (m. p. 53°), and a dihydriodide, $\text{C}_4\text{H}_7\text{I}_2 \cdot \text{CO}_2\text{H}$ (m. p. 90°), respectively.

These and other properties seem to prove that the acids $\text{C}_4\text{H}_4(\text{CO}_2\text{H})_2$ and $\text{C}_4\text{H}_5\text{CO}_2\text{H}$ are dicyclobutane derivatives, having respectively the formulæ—



197. "Optically Active Reduced Naphthoic Acids. Part I. Dextro- Δ^2 (or 3)-dihydro-1-naphthoic Acid." By ROBERT HOWSON PICKARD and ALLEN NEVILLE.

Dextro- Δ^2 (or 3)-dihydro-1-naphthoic acid is obtained from the 1-menthylamine salt, which is less soluble in ethyl acetate than the corresponding salt of the laevo-acid; it has $[\text{M}]_D + 370.4^\circ$ in chloroform. The transformation of the Δ^2 (or 3)-acid into the Δ^1 -acid in the presence of sodium hydroxide proceeds as a unimolecular reaction.

198. "Hydrazino-halides Derived from Oxalic Acid." By DOUGLAS ANDERSON BOWACK and ARTHUR LAPWORTH.

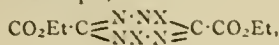
All the azo-derivatives of ethyl acetoacetate which have been examined by the authors are converted, on treatment with bromine or chlorine, into hydrazino-halides having the general formula Cl or $\text{Br} \cdot \text{C}(\text{CO}_2\text{C}_2\text{H}_5) : \text{N} \cdot \text{NHX}$ (compare *Trans.*, 1903, lxxxiii., 1114).

(NOTE.—The term "hydrazino" used for compounds containing the group $-\text{NH} \cdot \text{N} =$ corresponds with "imino," which refers to those including the radicle $-\text{N} =$).

The halogen atom in these compounds is very difficult to remove except in alkaline solution. With aqueous ammonia, the halogen is replaced by amidogen, whilst prolonged action of the agent leads to the further replacement of the ethoxyl group; the resulting compounds, $\text{NH}_2 \cdot \text{C}(\text{CO}_2\text{C}_2\text{H}_5) : \text{N} \cdot \text{NHX}$ and $\text{NH}_2 \cdot \text{C}(\text{CO} \cdot \text{NH}_2) : \text{N} \cdot \text{NHX}$ are yellow, and feebly basic in character. The members of the former class may be converted into the corresponding carboxylic acids, which lose carbon dioxide when heated.

Solutions of the hydroxides or carbonates of the alkali metals act very rapidly on the hydrazino-halides, and con-

condensation products which are probably dihydrotetrazine derivatives; for example,—



are obtained. These compounds form deep red crystals with a blue reflex.

199. "The Action of Nitrogen Sulphide on Organic Substances." (Part III.) By OLIVER CHARLES MINTY DAVIS.

The investigation of the action of nitrogen sulphide on the aldehydes has been continued, and it has been found that the reaction is not so general as was expected. Cinnamaldehyde, salicylaldehyde, and cuminaldehyde do not react to any extent, and the yields in other cases are very small. The nitrobenzaldehydes experimented with give the corresponding cyanidine derivatives, and an interesting example of steric hindrance is illustrated in the case of *o*-chlorobenzaldehyde, which is not appreciably decomposed, whereas the 1:4-compound readily yields the cyanidine derivative. A similar instance is noticed in the case of *o*-methoxybenzaldehyde, which furnishes a small amount of the cyanidine derivative, the 1:4-compound previously experimented with (*Trans.*, 1904, lxxxv., 1535) giving a good yield of the cyanidine, in addition to a sulphur compound and an anisamidine sulphate. Piperonaldehyde, on the other hand, in which the ortho-position with respect to the aldehyde grouping is unsubstituted, behaves in an analogous manner to anisaldehyde.

200. "The Action of Nitrogen Sulphide on Organic Substances." (Part IV.). By FRANCIS ERNEST FRANCIS.

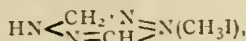
Nitrogen sulphide acts on acetic and propionic acids at their boiling-points with the liberation of sulphur dioxide and smaller quantities of nitrogen and the formation of the corresponding amides and diamides; in both cases ammonium sulphate and free sulphur are also formed.

The action on acetic anhydride and the halogen derivatives of acetic acid is very similar. Chloro- and bromoacetic acids give mixtures of their corresponding amides and diamides, di- and tri-chloroacetic acids only giving rise to di- and tri-chloroacetamides respectively.

That a deep-seated decomposition of the molecule takes place in these reactions is shown by the liberation of notable quantities of carbon monoxide, together with the other gases mentioned, and, further, the formation, in varying quantity, of the ammonium haloid salt corresponding with the halogen derivative employed.

201. "Tetrazoline." (Part III.). By SIEGFRIED RUHEMANN and RICHARD WILLIAM MERRIMAN.

The authors, who have undertaken this research with the view of investigating the remarkable properties of tetrazoline, and more especially of determining the constitutions of the two compounds which this base forms with methyl iodide (Ruhemann and Stapleton, *Trans.*, 1902, lxxxi., 261), have found that the colourless substance $\text{C}_3\text{H}_7\text{N}_4\text{I}$ combines with iodine to yield the blue additive product identical with the compound which is produced along with $\text{C}_3\text{H}_7\text{N}_4\text{I}$ by the action of methyl iodide on tetrazoline. It therefore has the composition $\text{C}_3\text{H}_7\text{N}_4\text{I}_3$ instead of $\text{C}_3\text{H}_9\text{N}_4\text{I}_3$, as previously stated. The resemblance of this additive product to the periodide of diazobenzene chloride led the authors to the view that $\text{C}_3\text{H}_7\text{N}_4\text{I}$ has the constitution—



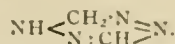
and therefore $\text{C}_3\text{H}_7\text{N}_4\text{I}_3$ the analogous formula—



It would therefore follow that the action of methyl iodide on tetrazoline,—



causes an isomerisation to—

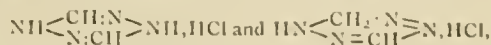


Such a transformation, as shown, takes place readily by the action of aldehydes on tetrazoline in the presence of piperidine, when compounds of the general formula—



are formed.

The authors have thus prepared a large number of condensation products, and have found that, although partially hydrolysed by hydrochloric acid, these solutions yield normal platinichlorides. The hydrolysis is complete on boiling with the dilute acid, and tetrazoline is formed together with aldehydes. The authors arrive at the conclusion that the hydrochloride of this base exists in two tautomeric forms,—



which are interchangeable. Platinic chloride is used as a means of recognising them, since the one modification forms the canary-yellow additive product, $(\text{C}_3\text{H}_4\text{N}_4)_2\text{PtCl}_4$, previously described, whilst the other yields the orange normal platinichloride, $(\text{C}_3\text{H}_4\text{N}_4)_2\text{H}_2\text{PtCl}_6$.

NOTICES OF BOOKS.

Handbook of Metallurgy. By Dr. CARL SCHNABEL. Translated by HENRY LOUIS, M.A., &c. Volume I. Second Edition. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1905.

This edition of Dr. Carl Schnabel's valuable work on Metallurgy has been carefully translated from the second German edition, which was brought up to date and published in 1902. This volume contains the elements copper, lead, silver, and gold, and in the case of each metal gives its properties, physical and chemical, the occurrence and composition of all its ores, and detailed accounts of the various extraction processes, attention being called to the differences in the practice of different countries. The book is fully illustrated with diagrams and plans, and will form a valuable addition to the metallurgist's library.

The Elements of Physical Chemistry. By J. LIVINGSTON R. MORGAN, Ph.D. Third Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1905.

In the preface to the third edition of this book the author acknowledges his indebtedness to Prof. Ostwald for suggestions and criticisms, and the influence of the writer of "Vorlesungen über Naturphilosophie" is clearly discernible in various parts of the book. This, however, is very far from being a drawback, and, indeed, beginners who find Prof. Ostwald's style rather difficult of comprehension, and those who are not capable of profiting by the study of his works at first hand, should be grateful for a work on the same lines but very much simpler. The book, which has undergone careful revision, specially emphasises the applications of physical chemistry, and endeavours to bring into prominence the practical rather than the theoretical side of the subject, while a good collection of exercises and problems for solution will be specially useful for those who are working without the aid of a teacher.

Transactions of the American Electrochemical Society. Volume VII. Philadelphia: The American Electrochemical Society. 1905.

This volume contains the proceedings of the Seventh General Meeting of the Society, held at Boston, Mass.,

and Cambridge, Mass., in April, 1905. The Address, delivered by President Henry S. Carhart, dealt with modern developments of the theory of electrolysis, and gave a very unbiassed view of several important steps in the revision of electrolytic theories; the Address is here reproduced in full, together with other papers read before the society. One of these, by H. R. Carveth and B. E. Curry, on "Chromium and the Electrolysis of Chromic Acid" is an important contribution to our knowledge of the oxidation products of chromium and of the properties of the metal, while another on "Colloids," by W. R. Whitney, summarises the subject in a very able manner. The reports of the discussions which followed the reading of the papers adds greatly to the interest and value of the book, and while none of the papers can be described as epoch-making, some of them deal with subjects of considerable importance, and throw light upon some of the many unsolved problems of electrochemistry.

Die Elektrolyse Geschmolzener Salze. Erster Teil: Verbindungen und Elemente. ("The Electrolysis of Fused Salts. Part I. Compounds and Elements"). By RICHARD LORENZ. Halle-a-S.: Wilhelm Knapp. 1905.

THIS volume forms the first part of a monograph on the electrolysis of fused salts, and deals with the elements and compounds, especially from the point of view of their qualitative preparation, while in subsequent volumes the application of Faraday's law and the theory of conductivity and electromotive forces will be discussed. The chief aim which the author has kept before him has evidently been the attainment of the utmost degree of completeness possible; he gives short abstracts of all the important work which has been done on the electrolysis of elements and compounds, and has for this purpose carefully searched patent literature, passing over purely technico-constructive aspects, but otherwise entering into the question very fully. The author's statements, as far as we have been able to test them, appear to be accurate and concisely put, and as a dictionary of this particular branch of electrochemistry the monograph seems to possess every good feature.

Recherches sur le Temps que la Précipitation met à Apparaître dans les Solutions d'Hyposulphite. ("Researches on the Time taken for the Appearance of Precipitates in Hyposulphite Solutions"). By GASTON GAILLARD. Paris: Gauthier-Villars. 1905.

THIS monograph describes the author's painstaking researches on the causes which influence the time required for the precipitation of hyposulphites, which he has investigated with great attention to the most minute details. He gives accounts of the results he has obtained when various factors were arbitrarily altered, such as the time taken in adding one solution to the other, mixing various neutral salts with either solutions, and the degree of freshness of the solutions, &c., and illustrates these and other results by curves, giving also a chart to show the change of colour of the precipitates and variations in their external appearance; the suggested application of the work is ingenious, though it is impossible not to foresee great difficulties in connection with it. The chapter on the relations which may exist between the time certain precipitates take to appear and the thermic phenomena which accompany them, though short, contains some interesting matter, while the author shows admirable judgment in summarising and drawing conclusions from his work.

The London Essence Co. announce that they have taken over the business of the Midland Essence Company, of Church Street, Newton Heath, Manchester, for the sale of Essences, Essential Oils, Perfumery, and all articles which interest Mineral Water Manufacturers, Manufacturing Confectioners, Perfumers, Soap Makers, &c. The premises of the aforesaid Company will be used as a dépôt to facilitate the delivery of goods to northern customers.

CHEMICAL NOTICES FROM FOREIGN SOURCES

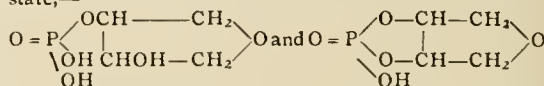
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 20, November 13, 1905.

Molecular Conductivity of Phosphoric Ethers.—P. Carré.—The author proposes to determine the molecular conductivity of some phosphoric acid ethers in order to investigate the modification that takes place in the conductivity of phosphoric acid by the partial substitution of

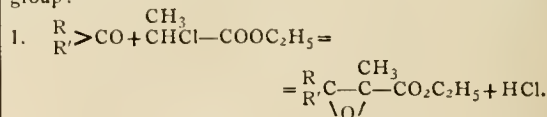
hydrogen by organic radicals, thus $O = P \begin{matrix} \text{OR} \\ \text{OH} \\ \text{OH} \end{matrix}$. He finds

that the monophosphoric ethers alone are sufficiently stable in aqueous solution for accurate determinations, which were made by Kohlrausch's method at a temperature of 25°, the inverse of the ohm being taken as the unit of conductivity. The ethers of ethyl and isobutyl alcohols, of glycol, glycerol, of erythran and mannide were prepared by the decomposition of their lead salts by means of H_2S . The author gives a table of his results, showing that for the same dilution the molecular conductivity of the ethers is appreciably higher than that of phosphoric acid, and depends on the number of carbon atoms in the radical R, and also on the function of this radical. For the same function the conductivity is less as R is greater. Thus ethylphosphoric acid has a higher conductivity than isobutylphosphoric acid, the same thing holding between glycol and glycerol derivatives, and between erythran and mannide phosphoric acids. Unfortunately for similar investigations on the di-ethers, these are not sufficiently stable in aqueous solution. But the author finds that, on determining the conductivity of a phosphoric mon-ether of a polyatomic alcohol partly transformed into a di-ether, it is higher than that of the mon-ether. Thus in erythranphosphoric acid, 35 per cent of which was in the di-ether state,—

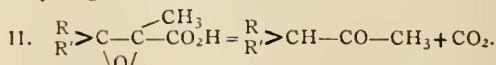


the values were 212 and 232 respectively for a dilution of 1 grm. molecule in 8. The author concludes, therefore, that the molecular conductivity of the di-ethers of phosphoric acid is probably higher than that of the mon-ethers, and that the ionisation of phosphoric ethers is considerably greater than that of phosphoric acid.

General Method for the Synthesis of the $\alpha\beta$ -Substituted Glycidic Ethers and of the Ketones.—Georges Darzens.—The author has given, in a previous note, a general method for the synthesis of β -disubstitution glycidic ethers by condensation of ketones with chloracetic ether, and now generalises this method by substituting α -chloropropionic ether, $CH_3 \cdot CHCl \cdot CO_2C_2H_5$. By this means he gets $\alpha\beta$ -tri-substituted glycidic ethers, a hitherto unknown group:—



By saponification these give very unstable acids, easily decomposing into ketones and CO_2 :—



This, therefore, is another method for the synthesis of ketones, and the mechanism of the transformation may be explained by imagining the formation of an oxide,

$R' > C - C < \begin{matrix} CH_3 \\ O \end{matrix}$, passing into the ketone. The author has prepared by this method glycidic acids from several ketones, and describes them as colourless liquids with slight odour, responding to all the chemical properties to be expected from their constitution. From the acids he has prepared five new ketones, and proposes to continue his researches with more complicated ketones and other homologues of chloroacetic ether.

MISCELLANEOUS.

"Mecker" Burners and Furnaces.—Messrs. W. and J. George, Ltd., 33—37, Hatton Wall, London, E.C., are supplying these new forms of burners and furnaces. There are two models: one, using gas at ordinary pressure, produces a homogeneous flame of very high temperature, much beyond that of the usual Bunsen, and available for a variety of purposes; the second model needs feeding with air under pressure, and with it a temperature of from 1350—1400° C. can easily be reached. By some simple arrangements of fire-clay covers and supports, these burners can be converted into really powerful furnaces, capable of fusing nickel and similar metals with ease. The burners are well and strongly made and are not expensive.

Lantern Slides of Natural History Objects.—Messrs. W. Butcher and Sons, of Camera House, Farringdon Avenue, London, E.C., are issuing a series of Junior Lecturer's Lantern Slides of Natural History objects (including British butterflies, moths, birds, and reptiles). They have been produced by a colour printing process, and great pains have been taken to make them as true to nature as possible, while at the same time the price is so low that they are brought within the reach of every student. They will be found especially useful in teaching natural history in elementary schools and for home study.

On the Reduction of Oxides, and on a Method of Preparation by Aluminium of the Compound $SiMn_2$.—E. Vigoroux.—Following the work of H. Moissan on the reduction of boric anhydride by magnesium, the author investigated the decomposition of silica by magnesium and by aluminium. In 1895 he showed:—(1) That the explosions obtained by Phipson, Gattermann, and others when investigating this decomposition was due to dampness; (2) that the application of a lighted match is sufficient to start the reaction throughout the whole mass; (3) that the heat generated is sufficient to melt the newly liberated silicon. In the course of his experiments the author noticed that, other things being equal, the oxide of the metal to be obtained should be chosen as high as possible, so that the heat necessary for the fusion may be greatest. For several years the author has reduced mixtures of oxides, and in this way he obtained $SiMn_2$. The reacting substances were prepared in the purest form: silica by the action of silicon chloride on water; brown oxide of manganese by the calcination of the dioxide obtained from the permanganate; aluminium was reduced to filings in the laboratory, and then freed from traces of iron by a powerful magnet. The crucible was lined with a thick layer of pure magnesia (0.5000 k.grm.) and the powdered dioxide of manganese and aluminium inserted. At the end of the reaction the contents were allowed to cool slowly. Hydrochloric and nitric acids easily attack the substance formed, and by the action of 2 per cent HCl followed by rapid washing with water acidulated with hydrofluoric acid, the author obtained crystals corresponding to the formula $SiMn_2$. This body is attacked by hot hydrochloric acid with the formation of silica. It is also affected by nitric acid, which differentiates it from that obtained by M. Lebeau.—*Comptes Rendus*, cxli., No. 19.

MEETINGS FOR THE WEEK.

- MONDAY, 11th.—Society of Arts, 8. (Cantor Lectures). "Measurement of High Frequency Currents and Electric Waves," by Dr. J. A. Fleming, F.R.S.
- TUESDAY, 12th.—Society of Arts, 8. "Historical Pageants," Louis N. Parker.
- Paradey Society, 8. "Physics of Ore Flotation," by J. Swinburne and G. Rudolf. "Concentration of Metalliferous Sulphides by the Flotation Process," by A. K. Huntington. "The Ions of Pure Water," by J. Walker.
- WEDNESDAY, 13th.—Society of Arts, 8. "The Commerce and Industries of Japan," by W. F. Mitchell.
- THURSDAY, 14th.—Society of Arts, 4.30. "Glimpses of French Canada," by the Hon. Rodolphe Lemieux, K.C. Society of Dyers and Colourists, 5. "Method for Production of Photographs on Silk," by P. J. Farrell.
- FRIDAY, 15th.—Physical, 7. (Royal College of Science, South Kensington). Exhibition of Electrical, Optical, and other Physical Apparatus.

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SCIENCE CLASSES, DAY & EVENING—

CHEMISTRY	ALEX. MCKENZIE, Ph.D., D.Sc.
PHYSICS	A. GRIFFITHS, D.Sc.
MATHEMATICS	E. H. SMART, M.A.
BOTANY	A. B. RENDEL, M.A., D.Sc.
ZOOLOGY	H. W. UNTHANK, B.A., B.Sc.
GEOLOGY & MINERALOGY	G. F. HARRIS, F.G.S.
METALLURGY, MINING, and ASSAYING	G. PATCHIN, A.R.S.M.

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Flexible Sandstone, 5/- to 50/- (See NATURE, June 23, 1904, page 185). Radio-Active Mud, 1/6 per bottle.
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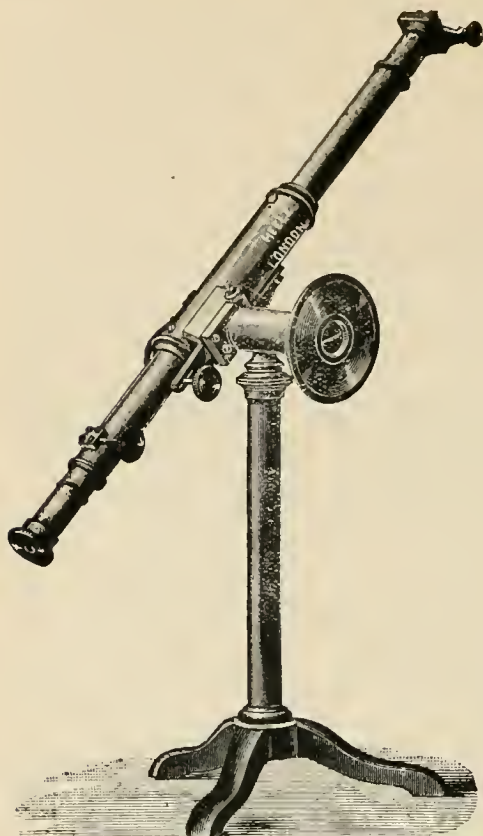
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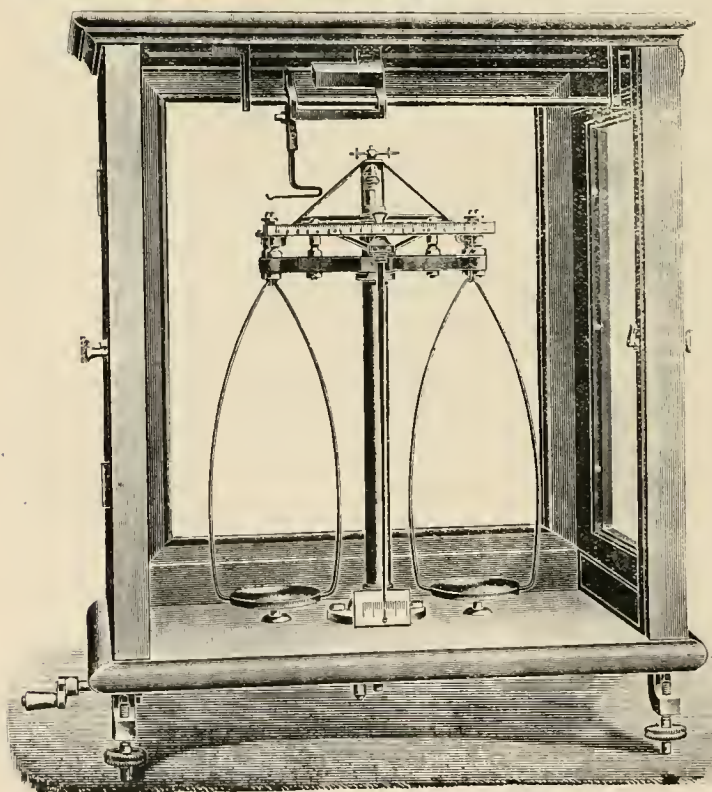
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THE CHEMICAL NEWS.

VOL. XCII., No. 2403.

ON SOME PHOSPHORESCENCE SPECTRA, INDICATING THE EXISTENCE OF NEW ELEMENTS.

By Sir WILLIAM CROOKES,

(Hon. D.Sc. (Oxford, Dublin, and Cape of Good Hope), F.R.S.

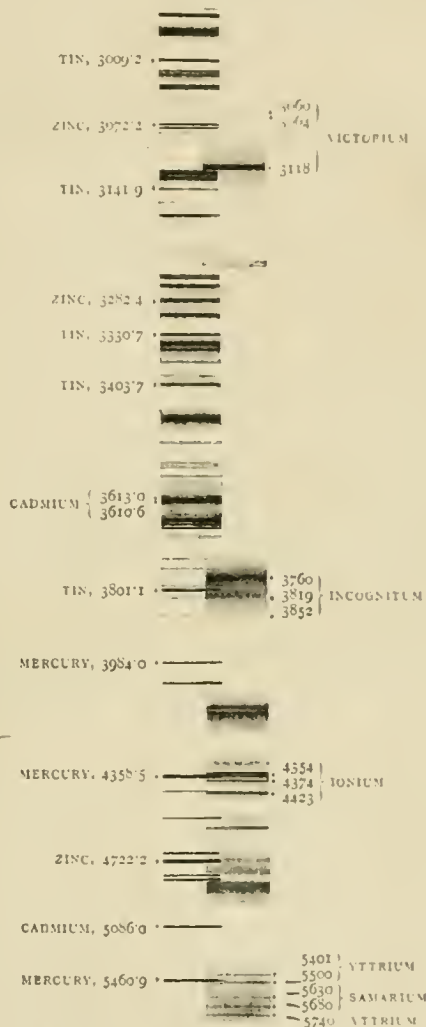
IN the course of my researches on the spectrum of the phosphorescent glow* emitted by some of the rare earths exposed to cathode rays *in vacuo*,† I have met with indications pointing to the existence of new elements. Assuming, as I think I am justified in doing from my previous work on yttrium, samarium, and victorium, that the presence of novel and special bands in a phosphorescence spectrum shown by a fractionation product of one of the yttrium or samarium group of earths may be a definite indication of a new body, I have met with at least two, and perhaps three, such groupings.

This method is an exceedingly delicate one.‡ It gives a spectrum of bands, more or less fine, easily recognised, but not so easy to measure definitely. The spectroscopist should be of low dispersion power and have a somewhat wide slit.

I can best illustrate my argument by calling attention to the accompanying drawing of the spectrum given by the phosphorescent glow of one of my fractions in which all these new groups, as well as some of those already described, are to be seen. The fine lines on the left spectrum are those of some well-known metals, photographed on the plate for the purpose of comparison, and having their wavelengths marked; the right spectrum is that given by the earth employed. Beginning at the bottom we first see the citron line of yttrium, 5740, then come the green pair of samarium, 5680 and 5630, and closely following these are the green pair of the earth I have called G β (terbium). A gap now intervenes, in which are some faint lines and bands not identified. We now approach the limit of vision where the deep blue bands of ytterbium, 4570 and 4530, are seen. Next come three very strong lines at 4423, 4374, and 4354, which I venture to say are due to the presence of a new earth, *ionium*. A rather hazy band follows, and then appear three other bands at 3852, 3819, and 3760; these almost certainly belong to a different body to that forming the other bands, but knowing little about it, except that its partial concentration by fractionation shows it to have chemical individuality, I call it *incognitum*. After a long gap we come to the very characteristic lines of victorium, at 3118, 3064, and 3060.

Did all these separate groups show themselves equally strong in all fractions I should say they were due to the same body, but this is not the case; for taking the better known bodies, yttrium, samarium, and ytterbium, we find the special lines due to these elements wax and wane *pari*

passu with the degree of richness in which they are present in the fraction under test. One fraction which may contain excess of yttrium shows the citron line with great intensity, while the other lines of samarium or ytterbium are comparatively feeble. Another fraction, on the contrary, may show scarcely any citron line, but is rich in the double greens of samarium or the ytterbium blues. Another may have all the others faint, while the greens of G β may shine out brilliantly, and, further, a fraction may be obtained in which scarcely any bands are seen but the rich blue of ytterbium. Now, in these instances, taking the



* "Contributions to Molecular Physics in High Vacua." *Phil. Trans. Roy. Soc.*, 1879, Part II., pp. 660-1.

† "On Radiant Matter Spectroscopy: The Detection and Wide Distribution of Yttrium." *Phil. Trans. Roy. Soc.*, 1883, Part III., p. 891. "On Radiant Matter Spectroscopy; Part II.—Samarium." *Phil. Trans. Roy. Soc.*, June 18, 1885; *Phil. Trans.*, 1885, vol. clxxvi., par. 167.

‡ "On some New Elements in Gadolinite and Samarskite, Detected Spectroscopically." *Proc. Roy. Soc.*, 1886, vol. xl., p. 509.

"The radiant-matter test applied to these phosphorescing bodies proves itself every day to be more and more valuable, and one of the most far-reaching and trustworthy tools ever placed in the hands of the experimental chemist. It is an exquisitely delicate test capable of being applied to bodies which have been separated approximately, but not yet completely isolated, by chemical means; its delicacy is unsurpassed even in the region of spectrum analysis; its economy is great, inasmuch as the test involves no destruction of the specimen, and its convenience is such that any given specimen is always available for future reference. Likewise the quantity of material is limited solely by the power of the human eye to see the body under examination. Beyond all these excellences is its trustworthiness. . . . During the years in which the test has been in daily use in my laboratory, I never once have been led to view its indications with suspicion. Anomalies and apparent contradictions have cropped up in plenty; but a little more experiment has always shown that the anomalies were but finger-posts pointing to fresh paths of discovery, and the contradictions were due to my own erroneous interpretation of the facts before me."

phosphorescent spectrum as a guide towards the mode and extent of fractionation, it is found not very difficult to concentrate the special band-giving earth to a greater and greater degree of isolation until we succeed in obtaining either yttrium, samarium, or ytterbium in a comparatively pure state.

Arguing from the known to the unknown, I find that, as I sub-fractionate certain portions of the rare earth fractions, I obtain earths in which one or other of the unknown groups already described grows fainter or stronger independently of the others or of the groups of lines attached to known elements. By this train of reasoning, therefore, I consider I am justified provisionally, and without undue insistence on what after all is only one of many necessary tests of newness, in saying that I am in possession of good

evidence pointing to the existence of two, if not of three, new bodies waiting to be isolated by chemical methods of fractionation.

[NOTE.—Since writing the above, I see that M. Urbain (*Comptes Rendus*, cxli., p. 954, Dec. 4th, 1905), in a paper to the Académie des Sciences, contends that the substance that I have called victorium may be a compound containing gadolinium.—W. C.]

THE ATOMIC WEIGHT OF TELLURIUM.

By A. GUTBIER.

IN order to purify the raw tellurium material, using first of all Hungarian tellurium and then 95 per cent tellurium from Dr. Theodor Schuchardt, of Gortitz, the author first separated the tellurium by reduction with sulphur dioxide, and dried it at a low temperature, after washing. The tellurium thus obtained was distilled *in vacuo*, and then part of the material was converted into telluric acid, and the rest into basic tellurium nitrate, in order to obtain a compound which could easily be purified by crystallisation. The first product, telluric acid, was prepared by evaporating a solution of the finely powdered tellurium in the purest nitric acid to dryness on the water-bath; the residue was then carefully dried at 105–110°, and suspended in the purest nitric acid. The mixture was then treated when boiling with a clear dilute solution of chromic acid, and when the last trace of tellurium dioxide had disappeared the oxidation was complete. The solution was then concentrated, and the tellurium separated out; the crystals thus obtained were heated with water on the water-bath, the liquid repeatedly filtered, and allowed to crystallise; and the crystals were re-crystallised from water. The clear colourless crystals thus obtained were completely soluble in hot water, without leaving the slightest trace of a residue. They were then dried *in vacuo*, and converted into the dioxide. The dioxide thus obtained dissolved in pure warm hydrochloric acid without yielding any chlorine, nor was any chlorine given off on boiling the solution. Thus it contained no trioxide.

The other part of the distilled tellurium was converted into the basic nitrate, which was re-crystallised twice, treated with absolute alcohol, dried, and converted into tellurium dioxide, which was also found to be perfectly free from trioxide.

The purified preparations were dissolved in hydrochloric acid, and after filtration the diluted solutions were saturated with the purest sulphuretted hydrogen free from arsenic. The precipitates were treated with freshly prepared carbon disulphide, and then with lukewarm water, filtered off, dried, pulverised, and extracted in a Soxhlet's apparatus with rectified carbon disulphide for thirty-six hours. After the residue had again been washed, dried, powdered, and extracted, pure tellurium could be isolated from it by fractionally distilling fourteen times *in vacuo*. This tellurium preparation consisted of brittle metallic particles with a metallic lustre and a crystalline fracture. The pure tellurium thus obtained was converted into the basic nitrate by Kothner's method, but as concordant results could not be obtained from this compound, even with the greatest possible care, it was converted into the dioxide as follows:—

A measured quantity of the nitrate was gently heated and allowed to cool, the operation being repeated until three consecutive weighings were constant. The tellurium was then determined:—

I. *By Reduction of the Dioxide by means of Hydrogen.*—The tellurium dioxide was weighed out in a porcelain boat, mixed with silver and quartz sand, and reduced with pure hydrogen in an air-bath at 100°; then the tube was heated to 350°, and the whole process was repeated until the weight of the tellurium was constant. In five

experiments the following atomic weights were found:—127.55, 127.60, 127.68, 127.59, 127.65.

II. *By Reduction of the Dioxide by means of Hydrazine.*

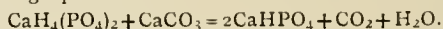
—The tellurium dioxide was weighed out into a platinum dish and treated at the ordinary temperature with pure dilute hydrochloric acid. Ten times the theoretical amount of freshly prepared hydrazine chlorhydrate was then added to portions of the tellurium solution in covered dishes, the mixture was gradually warmed on the water-bath, the temperature being kept at 50° for an hour, and then the water was boiled for an hour. The reduction was then complete. Three determinations gave the following values:—127.62, 127.67, 127.55.

The mean of all the eight determinations was 127.61. These results show that, however carefully tellurium is purified, the atomic weight is always found to be 127.6.—Abridged from *Liebigs Annalen der Chemie*, vol. ccxlii., p. 266.

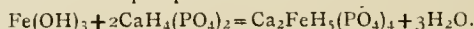
ACID VERSUS BASIC PHOSPHATIC FERTILISERS.

By W. F. SUTHERST, Ph.D., F.I.C.

PHOSPHORIC acid is applied to the soil in several forms, the principal of which are basic slag, bones, and superphosphate of lime, which, of course, are not of equal value as a plant food for the same soil, but are applied at the discretion of the farmer, who should know when and where these different sources of phosphoric acid should be spread. Superphosphate of lime being an acid salt naturally combines with all basic bodies in the soil in order to saturate or neutralise this acidity, such basic bodies being chalk, oxides of iron and aluminium, magnesia, &c. Should there be a large excess of chalk in the soil, we get a body formed, insoluble in water, but soluble in dilute organic acids—and consequently in root sap—represented by the following equation:—



But in most soils there is a large quantity of oxide of iron, generally in excess of the chalk, and under these conditions the soluble superphosphate is partly reverted to an insoluble iron and calcium phosphate:—



This double phosphate is practically insoluble in the acid root-sap, and therefore superphosphate reverted in this way is practically useless as plant food. Should there be very little of either chalk, oxide of iron, magnesia, &c., in the soil, the water-soluble phosphate is liable to be washed away from the sphere of the roots.

In the case of the bones, these are quite insoluble in pure water, but are dissolved slowly by the root-sap; as these have neither an acid nor basic reaction, their further discussion need not be undertaken.

With basic slag we get just the reverse reaction, for, being a compound of lime with phosphoric acid (the lime largely in excess), when mixed with water the mixture has an alkaline reaction. Its phosphoric acid is insoluble in water, but practically all soluble in dilute organic acids, and when mixed with the soil does not unite with any other bases, since it is fully combined already with a strong base, viz., lime. For this reason basic slag should be a more valuable manure generally than superphosphate, but its action is naturally slower, as the particles cannot come into such intimate contact with the rootlets as the distributed and reverted superphosphate. In most cases, however, an advantage can be expected by using the slag, especially on soils deficient in lime.

Some experiments on this subject were carried out on the College farm, when the effect of superphosphate, basic slag, and basic superphosphate (the latter being simply superphosphate supersaturated with lime) on the growth of mangels was tried. A piece of land was prepared, not too

rich in plant food, and on one portion superphosphate—at the rate of 400 lbs. per acre—added, in addition to 10 tons farmyard manure applied to each portion. To another basic slag was added in a sufficient quantity, so that its citric acid-soluble phosphoric acid equalled that in the superphosphate; the same with the basic superphosphate. The following yields were obtained:—

Manure.	Yield per acre.
1. Superphosphate	20 tons 12 cwt.
2. Basic slag	24 " 1 "
3. Basic superphosphate ..	24 " 19 "

The increased yield with the basic manures being about 20 and 25 per cent respectively.

The Agricultural College, Tamworth.

NEW RESEARCHES ON THE ATOMIC WEIGHT OF NITROGEN.*

By PHILIPPE A GUYE.

(Continued from p. 261).

I.—The Classic Gravimetric Methods do not admit of sufficient Accuracy to Determine exactly the Second Decimal of the Atomic Weight of Nitrogen.

IN order to prove this first thesis, I must first recall in a few words the principles upon which these methods rest, which are followed almost exclusively by all the scientists who are engaged upon the determination of the atomic weight of nitrogen:—

1. From the relation between ammonium chloride and silver the molecular weight of ammonium chloride is deduced, and by subtracting the atomic weights, $\text{Cl} + 4\text{H}$, the atomic weight of nitrogen is obtained; same method from the ratio $\text{NH}_4\text{Br} : \text{Ag}$.

2. By transforming a given weight of potassium chloride into nitrate, or *vice versa*, the molecular weight of KNO_3 is calculated, that of KCl being known; by subtracting the elements $\text{K} + 3\text{O}$, the atomic weight of nitrogen is obtained; the same method is applied to the ratios $\text{NaNO}_3 : \text{NaCl}$ and $\text{LiNO}_3 : \text{LiCl}$.

3. The transformation of the alkaline chlorates into nitrates, *i.e.*, the determination of the ratios $\text{KNO}_3 : \text{KClO}_3$ and $\text{NaNO}_3 : \text{NaClO}_3$ furnishes by an analogous method a new value for the atomic weight of nitrogen.

4. The transformation of silver into silver nitrate; *i.e.*, the ratio $\text{AgNO}_3 : \text{Ag}$, also the ratio $\text{AgCN} : \text{Ag}$, leads to new values for the atomic weight of nitrogen.

All these methods are indirect; they belong to the category of the methods called "of the second group"; the atomic weight found is given by an expression of the form:—

$$X = Ar - B,$$

where r is the atomic ratio determined experimentally (for example, the ratio by weight of ammonium chloride to silver for the first method mentioned above). A is a molecular weight, or an atomic weight supposed known (Ag in the example considered), and B a sum of atomic weights also supposed known ($\text{Cl} + 4\text{H}$ in the same example).

In order to judge of the accuracy of which these methods are capable, it is necessary to be exactly informed—(1) upon the accuracy realisable in the determination of the ratio r ; (2) upon the accuracy with which the quantities A and B are known.

Let us consider these points separately.

The atomic ratios r , utilised by the classic methods, are certainly among those obtained with the highest degree of agreement in this class of work, whether one examines the different determinations of a single experimenter or compares the means of the same ratio determined by different

observers. In the first case, the extremes of one series of observations are often contained between 18000 and 115,000; in the second case, the extremes between the means of several experimenters are generally between 1/3000 and 1/10,000. So as not to be too pessimistic, I will admit that these atomic ratios r are generally correct to $\pm 10,000$.

It is not the same for the atomic weights contained in the quantities A and B of the preceding relationship—

$$X = Ar - B.$$

These atomic weights are those of the elements Ag , Cl , Br , Li , Na , K , C . Nearly all are related more or less directly to the atomic weight of silver. It is necessary therefore to discover in the first place with what accuracy the latter is determined.

Those who have attempted to fix the most probable value of this atomic weight by utilising for the most part the same determinations, but with different combinations of the data of the experiments, have arrived at the following mean values:—

TABLE II.

	Ag for O=16.
Meyer and Seubert	107.93
Ostwald	107.94
Thomsen	107.93
Clarke (1897)	107.92
Clarke (1902)	107.95
Van der Plaats	107.92

The International Table for 1905 indicates $\text{Ag} = 107.93$.

The extreme range between these different values is about 1/3000. The accuracy with which the atomic weight of silver is known can therefore scarcely exceed $\pm 1/5000$. This is only to be expected when it is remarked that all the methods giving the atomic weight of silver depend upon that of oxygen, not directly, but always on the mean of two atomic ratios. Admitting that the error of each may be 1/10,000 (limit of the exactitude of the gravimetric atomic ratios), and that the errors add together, the want of certainty is again expressed by the fraction 1/5000.

This first point being admitted, it is evident that the atomic weights of the elements Cl , Br , Li , Na , K , which are only dependent upon that of silver, cannot be known with very great certainty. From the three atomic ratios it would appear logical to fix ± 13300 as the approximate degree of accuracy to which they are determined. In fact, the correction recently made in three of Stas's atomic weights, set forth in Table III., fully justify this conclusion.

TABLE III.

Elements.	Recent values for $\text{Ag} = 107.93$.	Values calculated by Clarke (1897).
Iodine	126.970	126.847
Chlorine	35.473	35.447
Sodium	23.008	23.048

The ranges are 1/1000 for I , 1/1360 for Cl , and 1/576 for Na !

Nevertheless, in order to simplify the calculation of the possible errors, we will admit that all the atomic weights to which that of nitrogen is referred are known correct to 1/5000. If this decision is found a little too rigid for silver, it must be remembered that it is very broad for the other elements which depend on it, Cl , Br , Li , Na , K .

These fundamentals being given, it is easy to calculate the error ΔN incurred in determining the atomic weight of nitrogen by one of the methods of the second group. In this estimation two extreme cases may first be mentioned:—(1) The errors are all of the same sign, and add together; (2) the errors are of alternate sign, so as to compensate one another as far as possible. Given that for a first approximation, the mean error attributable to this method is equal to the mean of these two extreme values both taken with the same sign, we arrive at a mean value of ΔN , to which it is interesting to fix the numerical magnitude. The following are the results obtained from this method of

* From the Bulletin de la Société Chimique de Paris, 1905.

calculation with the limits of accuracy above indicated, i.e., $\pm 1/10,000$ for the ratio r , and $\pm 1/5000$ for the atomic weights Ag, Cl, Br, Li, Na, K:—

TABLE IV.—*Limit of the certain Accuracy of the Atomic Weight of Nitrogen Determined by the various Classical Methods.*

Methods of the atomic ratios.	Mean ΔN .
1. $\text{NH}_4\text{Cl} : \text{Ag}$	± 0.013
2. $\text{NH}_4\text{Br} : \text{Ag}$	0.027
3. $\text{KNO}_3 : \text{KCl}$	0.020
4. $\text{NaNO}_3 : \text{NaCl}$	0.017
5. $\text{LiNO}_3 : \text{LiCl}$	0.014
6. $\text{AgNO}_3 : \text{Ag}$	0.039
7. $\text{KNO}_3 : \text{KClO}_3$	0.020
8. $\text{NaNO}_3 : \text{NaCl}$	0.017
9. $\text{AgCN} : \text{Ag}$	0.037
10. $\text{NH}_3 : \text{HCl}$	0.003

An examination of these numbers shows that not one of the classical methods (1 to 9) is susceptible, from the actual knowledge of the elements upon which they depend, of giving a value for the atomic weight of nitrogen of which the second decimal place can be guaranteed; the range of uncertainty in these methods lies between 1 and 4 units in the second decimal place; it would be greater still if a partial compensation of the errors had not been assumed, or if one took into account the real magnitude of the errors recently discovered in several atomic weights supposed known. (See Table III.).

It is not to be concluded that all the results of so much labour should be rejected wholesale, or that no method of the second group is capable of yielding accurate results. The mean value of ΔN from the method of Thomsen (ratio $\text{NH}_3 : \text{HCl}$), placed purposely at the end of the table, proves, on the contrary, that methods of the second group, suitably chosen, may yield perfectly accurate results.

What is certain is that classical methods are actually very ill chosen. I say "actually" because as a matter of fact there is a great disproportion between the accuracy of the atomic ratios employed and the accuracy with which the atomic weights supposed known are really so. When some day these atomic weights are determined in a more rigorous manner, the experimental results of the methods we have just discussed will very probably be utilisable afresh. The value of the atomic weight of nitrogen that is to-day deduced from them, is comparable to the topographical determination of a length by triangulation, in which the angles have been measured with a much greater accuracy than the base; when the base is known with a greater accuracy, the angular measurements will regain their full importance.

I believe in this way to have proved my first thesis:—

The classical gravimetric methods do not admit of sufficient accuracy for determining exactly the second decimal in the atomic weight of nitrogen.

Thus we are obliged, for the moment, to make an estimate of the most probable value of this atomic weight, whilst we are endeavouring to determine with certainty whether this value is 14.01 or 14.04.

(To be continued).

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 4th inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Lieut. E. P. C. Amphlett, F. Bailey, H. Behrens, J. Kennedy, J. N. Kerr, and Dr. E. M. Modi were elected Members. The Special Thanks of the Members were returned to Dr. Ludwig Mond, Ph.D., D.Sc., F.R.S., for his Donation of £500 to the Fund for the Promotion of Experimental Research at Low Temperatures. It was announced from the Chair that the Managers had elected Professor William Stirling, M.D., LL.D., D.Sc., Fullerian Professor of Physiology.

SOME OBSERVATIONS ON COLUMBIUM.*

By ROY D. HALL and EDGAR F. SMITH

(Concluded from p. 263)

Effect of Oxalic Acid.

ONE c.c. of E.

1 c.c. of D, or 1 grm. of oxalic acid in 50 c.c., required 2.6 c.c. of titanium solution C to show the characteristic pink colour, or 0.0000275 grm. of TiO_2 .

1 c.c. of reagent was adopted as the amount best suited to use, and was the amount taken in all of the following cases unless otherwise stated.

With 0.2 grm. of oxalic acid, 0.0000339 grm. of TiO_2 in 50 c.c. gave a pink colour.

With 0.5 grm. of oxalic acid, 0.0000275 grm. of TiO_2 was required to give the test for titanium.

1.0 grm. of oxalic acid required 0.0000244 grm. of TiO_2 to give the test.

In the presence of 2.0 grms. of oxalic acid, 0.0000244 grm. of TiO_2 gave a distinct pink colour in 50 c.c., while with 5.0 grms. of oxalic acid, 0.0000265 grm. of TiO_2 gave a colour.

The amount of oxalic acid seems to have little effect although the presence of the acid diminishes the delicacy of the test, but this is independent of the amount of the acid present when more than 0.1 grm. is used.

Effect of the presence of Hydrochloric Acid.

The solution of hydrochloric acid used was one part of concentrated acid to five parts of water.

With 1 c.c. of hydrochloric acid (1:5) and 1 c.c. of chromotropic acid in 50 c.c., 0.0000795 grm. of TiO_2 gave a distinct pink colour.

With 2 c.c. of hydrochloric acid (1:5), 0.00017 grm. of TiO_2 was required to give the colour.

When 5 c.c. of hydrochloric acid (1:5) was used, 0.0000424 grm. of TiO_2 gave a pink colour to 50 c.c.

Ten c.c. of hydrochloric acid (1:5) required 0.000848 grm. of TiO_2 for the colour.

Twenty c.c. of hydrochloric acid (1:5) required 0.00169 grm. of TiO_2 in 50 c.c. to give a definite test for titanium.

It may therefore be concluded that the destruction of the colour given by chromotropic acid is in proportion to the amount of acid present, so if this test is used hydrochloric acid should be absent.

Effect of Sulphuric Acid.

With 1 c.c. of sulphuric acid (specific gravity 1.435) 0.000318 grm. of TiO_2 was required to give a pink colour in 50 c.c. of solution.

With 2 c.c. of sulphuric acid 0.000742 grm. of TiO_2 was required to give the titanium test.

While more dilute solutions of sulphuric acid were not tried, it is evident that the effect of the sulphuric acid is roughly proportional to the amount of acid present, and that any appreciable amount of this acid seriously interferes with the delicacy of the test. The same is true of hydrofluoric acid.

In the presence of oxalic acid in any appreciable amount chromotropic acid will show 0.000025 grm. of TiO_2 in 50 c.c. very distinctly. Half that amount could be detected, but the colour is very faint, and its similarity to the colour possessed by the solution of chromotropic acid itself renders the detection of this amount uncertain. In making the test it is best to avoid the presence of free mineral acids, as they interfere, and generally in direct proportion to the amount of acid present. The neutral chlorides and sulphates are without effect, as Geisow has stated. It is probable that the colour developed in oxalate solution could be used to determine the amount of titanium present by comparison with the colour developed by known amounts of titanous acid, but this method would offer no especial advantage over the hydrogen peroxide method.

* *Proceedings of the American Philosophical Society*, 1905, xlv., p. 177.

The Action of Carbon Tetrachloride on the Oxides of Titanium, Columbium, and Tantalum.

According to Demarçay (*Comptes Rendus*, civ., 111) carbon tetrachloride vapour passed over the ignited oxides of columbium, titanium, and tantalum changes them to chlorides—in the case of titanium with the formation of an intermediate oxychloride.

Lothar Meyer (*Ber.*, xx., 681) found no action on oxide of titanium. He did not try the other two.

Delafontaine and Linebarger (*Journ. Am. Chem. Soc.*, xviii., 532) found that oxide of columbium was changed to oxychloride, CboCl_3 , with the formation of a small amount of the chloride. In the case of tantalum the oxide was not driven from the boat, but remained behind as a pasty mass, suffering no change to chloride. They suggest this as a possible separation of the two elements columbium and tantalum.

The vapour of carbon tetrachloride was found to act slowly on ignited titanic oxide at a low red heat, some chloride of titanium being continuously formed. In time all of the oxide was converted into chloride.

The oxide of columbium is readily acted upon by carbon tetrachloride even at a low red heat. The principal product is the white oxychloride. Some of the yellow chloride is simultaneously produced. It continues to be formed in small amounts as the oxychloride is sublimed in the vapours of carbon tetrachloride. Columbium oxide heated in a sealed tube with carbon tetrachloride is completely changed to chloride after several hours at $200-225^\circ$. The chloride dissolves in carbon tetrachloride, and separates from it in large, well-formed, needle-like crystals.

The action of the vapours of carbon tetrachloride on ignited oxide of tantalum is rapid, contrary to Delafontaine and Linebarger, converting it into chloride, which can be readily freed from the carbon tetrachloride, and thus obtained pure. If the carbon tetrachloride used contains traces of moisture, oxide will be produced by the decomposition of the chloride. This oxide dissolves in the fused chloride, and remains as a glassy mass upon sublimation of the chloride. Therefore, care should be taken in the dehydration of the tetrachloride used; otherwise the product will be contaminated with oxide. This seems to be the best method for the preparation of tantalum chloride in large quantities and in a high state of purity. The chloride is an excellent starting-out material for a re-determination of the atomic weight of tantalum, a number none too definite, as a study of the series of results obtained by Marignac (*Zeit. Anal. Chem.*, v., 478) by the analysis of potassium-tantalum fluoride and ammonium-tantalum fluoride will show.

The action of carbon tetrachloride on the oxide of columbium also affords an excellent method for the preparation of the oxychloride of that element. It is produced, however, in a very voluminous state, and mats together to a tough felt, completely stopping up any tube used in its preparation. When heated in a sealed tube it condenses on a warm surface to very compact lustrous silky needles. It is very difficult to remove the last traces of columbium pentachloride from this body. This may be done, however, by subliming it in a current of chlorine over ignited oxide, but as long as any carbon tetrachloride is present the columbium chloride will continue to be formed. To make the chloride of columbium it is necessary to have recourse to the action of sulphur monochloride on the oxide, or to act on the oxide with carbon tetrachloride in a sealed tube.

Properties of Columbium Chloride.

As already mentioned, columbium chloride is soluble in carbon tetrachloride, forming a yellow coloured solution. It is much more soluble when hot than when cold, and crystallises out on cooling in well-defined crystals. It is also soluble in sulphur monochloride, the solution saturated in the hot being red in colour, and depositing yellow crystals of the chloride on cooling. It dissolves in ether with a yellow colour. On evaporating this solution on a

water-bath a thick liquid remains, and an acid vapour is given off, but no crystals separate. Upon ignition the mass chars, then burns and leaves a residue of oxide. On passing dry ammonia gas into the ethereal solution of the chloride a heavy precipitate is formed. This is ammonium chloride and columbium nitride. On washing with water the ammonium chloride is dissolved out, leaving a white residue which reverts on ignition to oxide of columbium, and when boiled with sodium hydroxide gives off ammoniacal vapours, thus pointing to nitride of columbium, probably Cb_3N_5 .

Columbium chloride containing some sulphur monochloride was treated with benzene. The sulphur monochloride dissolved out, while the columbium chloride was decomposed, leaving an insoluble gummy mass. Chloroform dissolved the chloride readily, but the solution seemed to undergo decomposition on warming and evaporating, as the liquid became brown, and a brown powder separated. No crystalline product could be procured.

The chloride is also soluble in alcohol. In the cold there is no decomposition. On warming and concentrating the solution, acid vapours were given off, due perhaps, as H. Rose has suggested, to the formation of ethyl columbate. That there is no decomposition in dilute solution is shown by the formation of the compound $\text{CbCl}_3(\text{C}_5\text{H}_{11}\text{N})_6$, which was obtained on adding piperidine to the alcoholic solution (*Zeit. Anorg. Chem.*, xxxvi., 100). Other bases, such as aniline, pyridine, &c., gave addition products which were insoluble in the solvent.

The best solvent for columbium chloride is carbon tetrachloride. In this solution reactions should take place, as they do with other chlorides, in aqueous solution; also double chlorides, analogous to the double fluorides, should be formed by bringing together solutions of the chlorides in carbon tetrachloride.

Potassium Fluoxypercolumbate.

When potassium-columbium oxyfluoride is dissolved in 3 per cent hydrogen peroxide the solution acquires a yellow colour. When a saturated solution cools, a pasty mass of crystals separates. These are very hard to free from mother-liquor. When dry, they have only a faint yellow tint. On dissolving in water containing hydrogen peroxide the solution again becomes yellow in colour. The salt obtained in this way is potassium fluoxypercolumbate of the following composition:— $\text{K}_2\text{CbO}_2\text{F}_5 \cdot 11\text{H}_2\text{O}$.

Method of Analysis.

The potassium was determined as sulphate and the columbium as oxide in the usual way; that is, by expelling the fluorine with sulphuric acid, boiling with water, filtering out the insoluble columbium hydrate, and evaporating the filtrate to dryness and weighing the potassium sulphate after ignition.

The oxygen and water were determined in another sample by weighing a portion of the substance in a tube sealed at one end, covering it with a plug of ignited asbestos, connecting with a gas burette, and igniting. The oxygen was collected and measured, the tube was re-weighed, the loss being water and oxygen. The water was obtained by difference.

Analysis.—0.4004 grm. of the salt gave 0.1672 grm. of oxide and 0.2196 grm. of K_2SO_4 .

0.4432 grm. of the salt lost 0.0470 grm., which contained 17.9 c.c. of oxygen at 24° and under 742 m.m. pressure, or 0.0229 grm., the difference (0.0241 grm.) being water.

	Calculated	Found.
K_2SO_4	54.89	54.84
Oxide	42.28	41.84
O (active)	5.05	5.16
H_2O	5.68	5.44

This salt was obtained—and the above composition ascribed to it—by Piccini (*Zeit. Anorg. Chem.*, ii., 21).

He regarded it as a derivative of per columbic acid, and not an addition product of potassium-columbium fluoride and hydrogen peroxide, because the water was lost on heating at 100°, while the oxygen did not escape until the temperature reached 150°.

On crystallising this salt from concentrated hydrofluoric acid and hydrogen peroxide in the hope of getting a perfluoride, large plates were obtained, which were quite yellow in colour, with a green tint when dry. They did not seem to differ if little or much hydrofluoric acid was used. The crystals taken for analysis were obtained from a solution consisting of one-half hydrofluoric acid (48 per cent) and one-half hydrogen peroxide (3 per cent). They were dried between filter-paper and promptly weighed out for analysis.

Analysis.—0.7260 gm. of the salt gave 0.3274 gm. of oxide and 0.3982 gm. of potassium sulphate.

0.7482 gm. of salt lost 0.0784 gm. on ignition, *i.e.*, 29.1 c.c. of oxygen at 24° and under 742 m.m. pressure, or 0.0374 gm., the difference (0.0410 gm.) being water.

	Calculated.	Found.
K ₂ SO ₄	54.89	54.85
Oxide	42.28	42.34
O (active)	5.05	5.00
H ₂ O	5.68	5.48

Hence it may be concluded that the salt obtained from strong hydrofluoric acid is the same as that obtained when hydrofluoric acid is not used.

It would seem impossible to obtain a derivative of per-columbic acid which does not contain oxygen.

The salt separates from solutions containing hydrofluoric acid in large well-formed plates, which may be easily measured. They are much easier to handle than when crystallised from a solution free from acid. The crystals are always greenish yellow in colour.

Piccini states that the salt obtained by him had a slight yellow tint, but that this colour was completely removed by two re-crystallisations from hydrogen peroxide. The salt obtained above was re-crystallised six times from hydrogen peroxide containing hydrofluoric acid. The crystals from the last crystallisation were fully as highly coloured as those which had not been re-crystallised. They were then re-crystallised twice from hydrogen peroxide containing no acid. The resulting salt was practically colourless, but it dissolved in water and hydrogen peroxide with a yellow colour, which was intensified by the addition of hydrofluoric acid, and on evaporating again to crystallisation the crystals were as highly coloured as any obtained previously.

The oxide from the double fluoride originally used gave a colour equivalent to 0.4 per cent TiO₂. It was supposed that this colour was due entirely to titanium, and that the yellow colour of the solution and of the crystals of potassium fluoxypercolumbate was also due to this element. To test this supposition, 100 grms. of the purest potassium-columbium oxyfluoride was crystallised twice from strong hydrofluoric acid. The crystals obtained were decomposed with concentrated sulphuric acid, and the hydrate, after extraction with water, ignited to oxide. The colour which this oxide developed in oxalic acid solution with hydrogen peroxide was equivalent to 0.24 per cent of its weight of titanic acid. It was now heated in sulphur monochloride and converted into chloride. The latter, together with the excess of monochloride, was collected in a receiver, and the sulphur monochloride distilled out in the hope that any titanium tetrachloride present would be expelled with it. The chloride remaining after removing the sulphur monochloride was converted into oxide. It contained titanic oxide equivalent to 0.16 per cent. The oxide was again heated in sulphur monochloride and treated as before. After the second treatment the titanic oxide equivalent was 0.12 per cent, and the colour now developed was different. It was greenish yellow instead of yellow inclining towards red, which is characteristic of titanium. About 5 grms. of the oxide which had passed

through this treatment were changed to double fluoride and crystallised from hydrogen peroxide and hydrofluoric acid. Its solution in hydrogen peroxide was yellow, and its colour increased in intensity on adding hydrofluoric acid. The crystals from it were canary-yellow with a tint of green, differing in no respect from those previously obtained.

About 10 grms. of this yellow salt were next dissolved in water and hydrogen peroxide. This solution was distinctly yellow in colour. It was divided into two portions. To one portion 0.5 gm. of potassium-titanium fluoride was added. The colour in this portion became considerably deeper, but the excess of colour was completely discharged upon adding hydrofluoric acid, the two solutions becoming again identical in colour.

Potassium-titanium fluoride dissolved in hydrogen peroxide to a deep yellow-coloured solution. On cooling, crystals were deposited, which were not yellow but colourless when completely free from mother-liquor. The addition of hydrofluoric acid to the coloured solution completely destroys the colour, and in the presence of hydrofluoric acid the salt formed is white, resembling potassium-titanium fluoride. When air-dried it gives off neither water nor oxygen on ignition.

The only elements which give a distinctive colour in acid solution with hydrogen peroxide and which might occur here are titanium, vanadium, and molybdenum. Of these the first has been excluded and the second also, by reason of the colour which it gives (red to rose-red). There still remains molybdenum. Its colour in an oxalic acid solution with hydrogen peroxide is identical with that observed in the case of the columbium as free from titanium as it could be obtained. Although the columbium oxide used for these tests had passed through several manipulations which should remove molybdenum, such as fusion with sodium carbonate and sulphur, changing to chloride with sulphur monochloride and distilling off the more volatile portion, it was thought best to determine how much molybdenum would be required to give a test equal to that obtained from the purest oxide of the columbium at hand. To this end weighed amounts of molybdenum were dissolved in oxalic and sulphuric acids, and the colour developed with hydrogen peroxide compared with that obtained with a standard titanium solution of hydrogen peroxide.

1. 0.2780 gm. of molybdic acid developed a colour equivalent to 0.0048 gm. TiO₂, or 0.0058 gm. of molybdic acid will give a colour equal to that given under similar conditions by 0.0001 gm. TiO₂.

2. 0.0660 gm. of molybdic acid gave a colour equal to 0.0015 gm. TiO₂, or 0.0044 gm. of molybdic acid is equal to 0.0001 gm. TiO₂.

The variation in these results is due to the difficulty in matching the different shades as to intensity of colour. The average is about right, or 0.0050 gm. of molybdic acid is equivalent to 0.0001 gm. TiO₂. Calculating on this basis, the best oxide of columbium obtained, which gave a colour equivalent to 0.12 per cent TiO₂, would contain 6 per cent of MoO₃, if the colour was due to the presence of molybdenum, which would be impossible after the treatments through which the oxide has passed. It had been crystallised twice as potassium oxyfluoride, fused with sodium carbonate and sulphur, the tantalum removed, again crystallised as the oxyfluoride of potassium and twice from hydrofluoric as potassium-columbium fluoride, then changed to chloride in sulphur monochloride, the sulphur monochloride and the more volatile portions distilled off and rejected; again changed to oxide, and this treatment with sulphur monochloride repeated. The final oxide was converted into potassium fluoxypercolumbate and crystallised once from hydrogen peroxide and hydrofluoric acid. This salt was yellow in colour, and 0.3540 gm. of oxide from it, dissolved in oxalic acid, gave with hydrogen peroxide a colour equivalent to 0.000424 gm. TiO₂, or 0.12 per cent. At the most it could not have contained more than a bare trace of oxide of molybdenum.

0.3470 grm. of the oxide from the yellow fluoxypercolumbate was dissolved in oxalic acid and chromotropic acid and diluted to 50 c.c. It gave a very slight pink colour, about equal in intensity to the colour developed in 50 c.c. by 0.000025 grm. TiO_2 in the same amount of oxalic acid on treating with chromotropic acid. This would correspond to less than 0.01 per cent of TiO_2 , and is probably not very far wrong.

From these experiments it may safely be concluded that the colour produced in hydrofluoric acid solution of columbium with hydrogen peroxide is not due to the presence of titanium. Also it is probable that columbium itself gives a distinctive colour with hydrogen peroxide, equivalent to from 0.10 per cent to 0.15 per cent of its weight of TiO_2 , yet yellow-green instead of straw-yellow, as is given by titanium in dilute solutions. Possibly there may still be present some other element. For this careful search will be made.

Preparation and Analysis of the Yellow Oxide of Columbium.

Hydrated oxide of columbium, containing 10 grms. of oxide, was prepared by decomposing the double fluoride with sulphuric acid, evaporating off the excess of acid, and extracting with boiling water. This hydrate was washed repeatedly with boiling water and air-dried. It was covered with about 20 c.c. of concentrated hydrochloric acid and brought to boiling for several minutes, until all of the lumps had thoroughly disintegrated, when it was diluted to about three times its original volume with water. All but a few particles were dissolved. This solution was filtered and an equal volume of three per cent hydrogen peroxide added. It became yellow and after a few minutes a yellow precipitate appeared. The solution was allowed to stand over night. The precipitate was then filtered out, washed with cold water, in which it was insoluble, and air-dried.

Under the above conditions about one-quarter of the oxide in solution was precipitated by the hydrogen peroxide. If the remainder of the oxide in solution were recovered and dissolved in hydrochloric acid, as before, a fresh portion of it could be precipitated on adding hydrogen peroxide. The air-dried precipitate lost oxygen and water on ignition, and regained its white colour.

As the precipitation of the columbium was only partial it was best to be certain of the identity of the portion precipitated. To this end 2.5 grms. of the yellow oxide were obtained, ignited to remove the excess of oxygen, and changed to the potassium double fluoride. This analysed as follows:—

0.6822 grm. of the salt gave 0.3026 grm. of oxide and 0.3966 grm. of K_2SO_4 .

	Calculated.	Found.
Oxide	44.52	44.36
K_2SO_4	57.81	58.14

Hence the compound obtained is a derivative of columbium.

Columbium is not precipitated from the solution remaining after the yellow precipitate has been filtered out, by an excess of ammonium hydroxide, until the hydrogen peroxide in the solution has been destroyed.

Analysis of the Yellow Precipitate.—0.1917 grm. of sample gave 0.1298 grm. of Cb_2O_5 .

0.2556 grm. of sample gave 7.8 c.c. of oxygen at 22°, and under 741 m.m. pressure, equal to 0.0101 grm.

	Percentage.	Ratio.
Cb_2O_5	67.71	1.000
O (active)	3.95	0.984
H_2O (difference) ..	28.34	6.240
	100.00	

This corresponds to $\text{Cb}(\text{OH})_6$, or to $\text{Cb}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$.

Melikoff and Pissarjewsky (*Zeit. Anorg. Chem.*, xx., 340) obtained a percolumbic acid of the formula $\text{HClbO}_4 + n\text{H}_2\text{O}$, by heating columbium hydrate with 30 per cent hydrogen peroxide on a water-bath. They also obtained it by adding sulphuric acid to a solution of sodium percolumbate, dialysing out the excess of sulphuric acid and the potassium sulphate, then evaporating the clear yellow solution to dryness on a water-bath. They describe it as a yellow amorphous powder, insoluble in water.

The colour of these higher oxides seems characteristic of columbium, and is certainly not due to the presence of titanium. The hydrate obtained by Melikoff and Pissarjewsky contained twice as much active oxygen, in proportion to the columbium, as did the hydrate obtained during this investigation.

Difference in Solubility of Double Fluorides.

It is of interest to note that the solubility of potassium-titanium fluoride is increased upon the addition of hydrogen peroxide, while that of the potassium-columbium oxyfluoride is decreased. In hydrofluoric acid this order is reversed, the columbium salt becoming more soluble and the titanium salt less soluble. This suggests alternating these solvents in the crystallisation of columbium and potassium double fluorides as one of the best means for removing titanium.

Re-crystallisation from hydrofluoric acid in the form of $\text{K}_2\text{C}_2\text{F}_7$ will remove tin and probably also tungsten from impure potassium-columbium oxyfluoride. Two re-crystallisations from that solvent are sufficient to give an oxide, the ignition of which in a platinum crucible gave no stain on the crucible. If partially dried oxide wrapped in the filter-paper be ignited directly in a platinum crucible the presence of a stain on the crucible after removing the oxide will be a very delicate test for tin. It is likely that when tin is removed by crystallisation tungsten is also, if they are present in about equal amounts and in such cases where the total amount is very small. The procedure would remove the necessity for the tedious sodium carbonate and sulphur fusions used in this work.

Behaviour with Precipitants.

Pennington (*Journ. Am. Chem. Soc.*, xviii., 38) noted that disodium-hydrogen phosphate gave no precipitate in a solution of potassium-columbium oxyfluoride, while it completely precipitated titanium from a solution of its double fluoride. This was studied briefly in order to determine if it might not serve as a quantitative separation of columbium from titanium. It was found that when the reagent was added to a solution containing a large excess of columbium and only a little titanium, no precipitate was produced even on prolonged boiling. If the amount of titanium was increased slightly, both the titanium and the columbium were completely precipitated by the disodium-hydrogen phosphate. This reagent, therefore, does not separate the two elements.

Geisow found that an alkaline formoxime solution precipitated zirconium and titanium, but did not precipitate columbium.

Formoxime, or its polymerisation product, was prepared by bringing together solutions of the calculated quantities of formaldehyde, sodium carbonate, and hydroxylamine hydrochloride. The resulting solution gave no precipitate when added to a solution of titanium as double fluoride, zirconium as double fluoride, or to a solution of columbium double fluoride. Further, after the addition of the formoxime solution, ammonium hydroxide failed to give a precipitate with any of the solutions noted above. It did, however, give a precipitate with tantalum double fluoride, but this was only partial.

The statement of Geisow that titanium and zirconium can be separated from columbium by means of an alkaline formoxime solution was not verified. The precipitation with tantalum is only partial, and not complete as stated by him.

It was noted (*Journ. Am. Chem. Soc.*, xxvi., 1248) that potassium iodate gave a complete precipitation in a solution of potassium-titanium fluoride, and no precipitate with a solution of columbium double fluoride. Potassium indate, free from periodate, was prepared, and it was found to give no precipitate with either columbium or titanium, except in acid solution, when both were precipitated. A solution of a periodate was not tried.

NOTICES OF BOOKS.

Chemisch-technische Untersuchungsmethoden. ("The Chemical Examination of Technical Products"). Edited by Dr. GEORG LUNGE. Vol. III. Fifth Edition. Berlin: Julius Springer. 1905.

THE third volume of the latest edition of this encyclopædia of technical chemistry deals amongst other subjects with oils, caoutchouc, sugar, starch, alcoholic beverages, organic colouring matters, &c., all the articles having been revised and brought up to date. Some of the papers are entirely new and written by new authors; for instance, oils, fats, and waxes are treated very exhaustively by Dr. J. Lewkowitsch, caoutchouc and objects made of it by Dr. Fritz Frank and Dr. Eduard Marckwald, and beer by Prof. C. J. Lintrner; while other sections, such as those on mineral oils and organic colouring matters, have been considerably enlarged.

Gmelin—Kraut's Handbuch der Anorganischen Chemie. ("Gmelin and Kraut's Handbook of Inorganic Chemistry"). Seventh Edition. Vol. I., Part I. Edited by A. HILGER and C. FRIEDHEIM. Heidelberg: Carl Winter. 1905.

THE revision of this handbook of inorganic chemistry, which is probably unequalled for completeness in any other language, has been most thoroughly performed, to judge by the first part of Volume I. of the seventh edition which has just appeared. Several workers have collaborated for the purpose of collecting fresh information and critically examining the text, and they hope to complete the issue of this latest edition within three or four years, so that those who now begin to purchase the parts as they appear will not have very long to wait before they are in possession of the whole work, which will be found of unique value as a book of reference.

Traité Pratique d'Electrochimie. ("Practical Treatise on Electrochemistry"). By RICHARD LORENZ. Remodelled from the German Edition by GEORGES HOSTELET. Paris: Gauthier-Villars. 1905.

THE French edition of this work is more than a mere translation of the original, the author and translator believing that the adoption of a somewhat different method of presenting the subject might add to the value of the work from the point of view of French readers. The book is divided into three parts; the first deals with the elementary laws of electrochemistry, and the second with the theory of the electrolysis of aqueous solutions, while the third and shortest part is devoted to applied electrochemistry, electrochemical analysis, and the production of substances by electrochemical means. The treatment throughout is quite elementary, and the experimental details are clearly described, so that the beginner if he follows the instructions should find no difficulty in obtaining satisfactory results; the theory of electrochemistry is also explained fully enough to enable the student to interpret his results correctly.

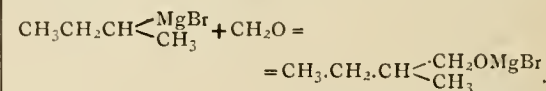
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 21, November 20, 1905.

Action of Silicon Chloride on Iron.—E. Vigouroux.—Frémy has shown that, by this action, a silicide can be obtained crystallising in octahedral crystals, insoluble in acids and in aqua regia, having the composition Si 33 per cent, Fe 67 per cent, leading to the formula SiFe. The author has shown, by acting on other metals with the same chloride, that there is reason to consider the condition of formation of the compound SiFe₂, made known by the investigations of H. Moissan, a compound which is formed during the same reaction. As the result of three separate determinations, in which SiCl₄ was passed over reduced iron raised to just under red heat, the author obtained the silicide subliming in the delivery tube, and on analysis giving Si 20 per cent, Fe 80 per cent, leading to the formula SiFe₂. The conclusions arrived at by the author are as follows:—1. The decomposition of silicon chloride by iron takes place at a temperature below red heat. 2. The action is complete; that is to say, it takes place without the formation of the lower chlorides of silicon (since only SiCl₄ is found in the condensation apparatus). 3. The nascent silicon combines completely with the iron, leading to the formation of the alloy containing 20 per cent of silicon. 4. At this point all silication ceases under these conditions of temperature, and the reaction corresponds to the well-known formation of Fe₂Si. 5. The reaction can be represented thus:—SiCl₄ + 4Fe = Fe₂Si + 2FeCl₂. The author proposes to continue his investigations at higher temperatures, in order to ascertain the conditions of formation of the higher ferro-silicides.

Preparation of Racemic Amyl Alcohol.—P. Freundler and E. Damond.—Racemic amyl alcohol, $\text{C}_2\text{H}_5 > \text{C} < \begin{smallmatrix} \text{H} \\ \text{CH}_3 \end{smallmatrix} \text{CH}_2\text{OH}$, has up to the present only been obtained by the reduction of tiglic aldehyde and by the racemisation of the active alcohol. These two methods are not very useful, on account of the rarity of the initial compounds. The authors state that this alcohol can be prepared under much better conditions by a similar process to that of M. Locquin in the case of ordinary isoamyl alcohol, $(\text{CH}_3)_2\text{CH}.\text{CHCH}_2\text{OH}$. The method consists of condensation of the magnesium derivative of secondary butyl bromide with trioxymethylene:—



The butyl bromide was obtained by the action of phosphorus tribromide on secondary butyl alcohol obtained from the reduction of methylethylketone by the method of M. Sabatier. The retarding effect of certain substances on the formation of derivatives of magnesium has been recently shown by MM. Bischoff and Ahrens. The authors have shown this in many other cases in which this influence, far from being favourable, as for amyl alcohol, prevents completely the action of the halogen derivative on the magnesium. Especially does this happen in the preparation of triphenylcarbinol, when the commercial ether at 65° is used without acting upon it with sulphuric acid. This ether retains, indeed, aldehyde and sulphur compounds, from which it cannot be freed even by prolonged contact with sodium.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxviii., No. 14, 1905.

Action of Sulphurous Acid on the Triphenylmethane Dyes.—Karl Dürschmabel and Hugo Weil.—The authors have found that with *p*-rosaniline sulphurous acid forms compounds which possess the composition of normal salts, and they have succeeded in isolating an acid sulphite, $C_{19}H_{19}N_3O + H_2SO_3$, which is a faint pink. This compound is crystalline, and exactly resembles a rosaniline base. On treating with dilute soda solution or on boiling with water, a neutral rosaniline sulphite is obtained which, when dried at 100° , has the composition $(C_{19}H_{17}N_3)_2H_2SO_3$ (without water of crystallisation). This substance forms metallic-looking crystals, and belongs to the type of quinoid salts. Besides these two sulphites, the authors have obtained a third colourless substance, $C_{19}H_{17}N_3 \cdot H_2SO_4 + \frac{1}{2}H_2O$, which apparently belongs to the class of leuco-sulpho acids, described by Hantzsch and Osswald.

Decomposition of Chromic Acid by Hydrogen Peroxide.—E. H. Riesenfeld.—If a few drops of hydrogen peroxide are added to an acid chromic acid solution, the chromic acid is reduced directly to a salt of chromic oxide. No trace of a blue colouration is to be observed when this reaction occurs, the reddish yellow colour of the solution merely becoming temporarily darker, while oxygen is energetically evolved. If, however, a few drops of a chromic acid solution are added to an acid solution of hydrogen peroxide an intense blue colour appears, and afterwards changes to green, oxygen being evolved. Berthelot has already observed that the quantities of oxygen evolved in the two cases are not equal. In the first case the reaction proceeds according to the equation $2CrO_3 + 3H_2O_2 = Cr_2O_3 + 3H_2O + 3O_2$, and in the second according to the equations $Cr_2O_6 + H_2O_2 = Cr_2O_7 + H_2O$, $Cr_2O_7 + 4H_2O_2 = Cr_2O_3 + 4H_2O + 4O_2$. The end of the reaction was very difficult to determine in both cases. The experiments of Berthelot and other investigators show that the larger the excess of hydrogen peroxide used the larger is the amount of oxygen obtained. The author has found that when an excess of chromic acid is present it is decomposed by hydrogen peroxide according to the above equation in the same way as with permanganate. When chromic acid is decomposed by excess of hydrogen peroxide a perchromic acid of the formula H_3CrO_8 is formed as an intermediate product; when its salts are dissolved in acids they yield an intense blue colouration. On reducing the acid to chromic oxide salt five atoms of oxygen are set free for every atom of chromium. The amount of oxygen found experimentally is somewhat smaller than this, so that it is possible that besides the perchromic acid H_3CrO_8 an acid less rich in oxygen is formed, e.g., H_3CrO_7 . In alkaline solutions it may be assumed that the salts of the acid H_3CrO_8 are first formed. These salts are yellow or yellowish brown in dilute aqueous solution, and are decomposed in alkaline solution, yielding chromates, heat being evolved.

Boiling-points of the Alkali Metals.—Otto Ruff and Otto Johannsen.—Carnelley and Carleton Williams found that the boiling-point of potassium lies between 719° and 731° and that of sodium between 861° and 950° . Perman, employing a different method, found for sodium $743-746^\circ$ and for potassium $656-674^\circ$. The authors have now further investigated this subject, and have also determined the boiling-points of the other alkali metals, using a method of direct distillation. This could be performed (except in the case of lithium) without much difficulty, for the alkali metals do not attack iron at their boiling-points and can therefore be distilled in closed wrought iron vessels. The temperature of the vapours was determined thermoelectrically. The distilling apparatus consisted of a wrought iron tube, which widened out into a bulb at its lower end. The upper end could be closed by means of a screw-stopper through which a steel tube containing the thermo element could be passed. This retort was heated in a Rössler's gas furnace, special precautions being taken

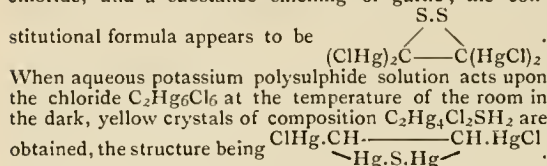
to prevent overheating the neck of the retort. A platinum-platinrhodium thermo element was used to measure the temperature. Commercial sodium was used without any preliminary purification, but potassium was first fused under petroleum. Rubidium and caesium were prepared by heating their hydroxides with magnesium, and were then fused under petroleum. Lithium was prepared by fusing and electrolysis a mixture of equal parts of lithium chloride and potassium chloride in a Muthmann's electrolysis vessel, a rod of graphite being used as anode and two iron wires as cathodes. The following boiling-points were found at atmospheric pressure:—(760 m.m.): Caesium, 670° ; rubidium, 696° (698.1°); potassium, 757° (759°); sodium, 877.1° (879°); lithium, above 1400° . The temperatures given in brackets are the limiting temperatures which were obtained with more rapid boiling. The boiling-point of lithium could not be determined, as, contrary to previous statements, even the heat of the gas furnace was not sufficient to cause it to vapourise. At about 1400° about half the metal used remained unchanged in the retort, while the rest was converted into hydride or nitride. Even when the temperature was raised to such an extent that the wrought iron retort fused, the lithium was not vapourised, so that its boiling-point lies above 1400° . If the atomic weights of the alkali metals are taken as abscissae and their boiling-points as ordinates, a curve is obtained which rises gradually from caesium through rubidium to potassium, then somewhat more rapidly to sodium, and thence very rapidly to lithium. The curve is similar to the melting-point curve of these metals, but it does not enable the boiling-point temperatures to be expressed by a simple mathematical formula as a function of the atomic weight.

Preparation of Pure Ethyl Alcohol.—L. W. Winkler.—The following method seems specially suitable for the purification of ethyl alcohol for scientific purposes. To remove the aldehyde present silver oxide is added to the alcohol, and also some alkali hydroxide; after some days the alcohol will be found to be quite free from aldehyde, which is oxidised by the silver oxide to acetic acid, which then combines with the alkali. To remove water from alcohol metallic calcium is used. The metal in the form of turnings is allowed to act upon the alcohol in a distilling apparatus which is warmed on the water-bath. After some hours the alcohol is distilled off; it generally then contains 99.9 per cent of pure alcohol. To remove the last traces of water it is again distilled with calcium.

Electric Preparation of some New Colloidal Metals.—The Svedberg.—The author has modified Bredig's method of preparing hydrosols, using organic liquids, the metal foil being suspended in the liquid. Iron or aluminium were employed for the electrodes. Thus he very easily obtained colloidal tin, gold, silver, and lead. This method, however, is not applicable in the case of some metals; for instance, it is not possible to bring aluminium foil into solution, although the phenomena which occur are apparently exactly similar as regards the formation of sparks, &c. For these metals a second method was employed, i.e., the potential was raised and the current strength correspondingly reduced. A glass condenser of 225 sq. c.m. surface was connected in parallel in the secondary circuit of a spark inductor and the secondary pole connected with electrodes which were immersed in a porcelain dish. The metal was placed in the dish, either granulated or cut up into wire, and the liquid over it. On stopping the current a brilliant spark display occurs between the particles, the liquid becomes coloured, and in a few minutes a dark coloured solution is obtained. It is naturally an advantage to use electrodes and metallic particles of the same metal, but the influence of the electrodes is very small. By this second method colloidal magnesium was formed as an olive-green solution in absolute ethyl ether. The author has also succeeded in obtaining the alkali metals in the colloidal state. They are exceedingly unstable. Colloidal sodium is violet, and colloidal potassium blue-violet, both in ligroin, ligroin-naphthalene, and

ethyl ether. The author has also employed his method to prepare specimens of other metals which are already known in the colloidal state.

Action of Ethane Mercarbide on Alkali Sulphides and Sulphur Chloride.—K. A. Hofmann and H. Feigel. —By the action of alcoholic alkali on mercuric oxide, $C_2Hg_6O_4H_2$ is produced; it is very stable towards acids and alkalis, but on heating to 200° or on rubbing the dried substance between paper at the ordinary temperature it explodes violently. Nitric acid, chromic acid, perchloric acid, chloric acid, and bromic acid have no action upon this substance beyond forming salts in which the molecule $C_2Hg_6O_4H_2$ functions as a base. If this base is shaken for some days with 10 per cent sulphur chloride-benzene mixture a yellow crystalline product, $C_2Hg_4Cl_4S$, is obtained; this when heated gives carbon, mercurous chloride, and a substance smelling of garlic; the constitutional formula appears to be



Both the mercury-carbons bonds of the hexamercuric ethane and also the other mercury bonds are very firm. The cyanide of tetramercuric ethane, $\text{CN.Hg(Hg):C:C(Hg).Hg.CN}$, is prepared by warming $C_2Hg_6O_4H_2$ with aqueous potassium cyanide solution. If aqueous potassium polysulphide solution is added to this cyanide, the CN groups and half the mercury split off, a yellow precipitate of $C_4Hg_4SH_6$ being obtained; the constitutional formula of this substance is $(\text{Hg:CH.CH}_2\text{.Hg})_2\text{S}$. Those carbides of mercury all illustrate how firmly mercury atoms can be bound to carbon.

MISCELLANEOUS.

Catalogue of Scientific Apparatus.—We have received from Messrs. Gallenkamp and Co., Ltd., 19—21, Sun Street, Finsbury, London, E.C., a new and very fully illustrated Catalogue of General Chemical and Scientific Apparatus. Besides the description of a vast number of pieces of apparatus, the book contains some very useful tables, equivalent measures, comparison between inches, millimetres, and wire gauge, electrical measures, &c. Messrs. Gallenkamp and Co. are agents for Sartorius Balances and Weights, and some beautiful instruments of this and other makes are included. The book is carefully indexed, and seems to contain everything that can be needed in the way of apparatus for the teaching and practice of chemical and physical science.

Royal Institution.—The following are the Lecture Arrangements at the Royal Institution, before Easter:—A Christmas Course of six illustrated lectures, adapted to a juvenile auditory, by Professor H. H. Turner, on "Astronomy"; Professor E. H. Parker, three lectures on "Impressions of Travel in China and the Far East"; Professor William Stirling, six lectures on Physiology subject; Dr. J. E. Marr, three lectures on "The Influence of Geology on Scenery" (The Tyndall Lectures); Rev. Canon Beeching, two lectures on "Shakespeare"; Mr. Benjamin Kidd, two lectures on "The Significance of the Future in the Theory of Evolution"; Mr. H. B. Irving, two lectures on "The English Stage in the Eighteenth Century"; Mr. Francis Darwin, three lectures on "The Physiology of Plants"; Professor B. Hopkinson, three lectures on "Internal Combustion Engines" (with Experimental Illustrations); Mr. J. E. C. Bodley, two lectures on "The Church in France"; Mr. J. W. Gordon, two lectures on "Advances in Microscopy"; Mr. M. H. Spielmann, two lectures on "George Frederick Watts as a Portrait Painter"; and Professor J. J. Thomson six

lectures on "The Corpuscular Theory of Matter." The Friday Evening Meetings will commence on January 19, when Professor J. J. Thomson will deliver a Discourse on "Some Applications of the Theory of Electric Discharge to Spectroscopy." Succeeding Discourses will probably be given by Professor S. P. Thompson. Mr. H. F. Newall, Mr. W. C. D. Whetham, Dr. R. Caton, Dr. Hutchison, Sir Andrew Noble, Bart., Professor P. Zeemann, Mr. W. B. Hardy, and other gentlemen.

University College, London.—A course of Biological Chemistry, suitable for candidates in Branch F of the Institute of Chemistry, and for B.Sc. Honours Candidates, will be held by R. H. Aders Plimmer, D.Sc., in the Physiological Department during the Second and Third Terms (January to July). The class will meet on Mondays, Wednesdays, and Fridays from 10 to 5. The subjects dealt with will include the preparation, properties, and actions of enzymes; the preparation of their principal products; the preparation and estimation of the principal carbohydrates; the preparation, crystallisation, and properties of animal and vegetable proteids, and their disintegration products. Fee for course, 10 guineas (exclusive of expense of materials). A Special Course in the methods employed for the study of Bacteria, Yeasts, and Moulds will be held, if required, in the Bacteriological Department of the College during the Second and Third Terms.

Memorandum from the White Lead Corroders' Trade Section of the London Chamber of Commerce.—*The Merchandise Marks Act, 1887.*—The White Lead Corroders' Section of the London Chamber of Commerce desire to call the attention of such of our readers who may be users of White and Red Lead, whether dealers, painters and decorators, plumbers, carpenters, and wheelwrights, &c., to the steps they have taken in the past, and are still taking to secure proper protection to the public as regards the quality of the White and Red Lead they may have necessity to use. It has come to the knowledge of the Section that users of White and Red Lead, especially small buyers, have been misled in buying as "Best," "Genuine," or other term indicating the highest quality, a lead which on analysis has been found to be adulterated, and the Section desire to draw attention to the fact that it is a distinct breach of the Merchandise Marks Act, 1887, to describe and sell as "Best," "Genuine," or other similar term, any White or Red Lead which contains any adulterant such as barytes, lime, or any other foreign added matter. The penalties attaching to the use of misleading terms under the Merchandise Marks Act are unusually heavy, and even go so far as imprisonment with hard labour, so that it behoves everyone in the trade to take due precautions against their offering or having in their possession for sale, White or Red Lead which bears a misleading description within the meaning of the Act. In this connection the White Lead Section of the Chamber are prepared to examine and report on, *free of charge*, any sample of White or Red Lead bought as "Best," "Genuine," or other term indicating of the highest quality, if a small sample of the same is sent to "The Inspector," White Lead Corroders' Trade Section, London Chamber of Commerce, Oxford Court, London, E.C. A half-pound sample will be sufficient for the purpose of analysis. It should be mentioned that the Section in their endeavours to protect the small user have undertaken several cases in different parts of the country, under the Merchandise Marks Act, against firms selling adulterated Lead as "Best" or "Genuine," and, with one exception, convictions have been obtained and heavy penalties inflicted. In this connection the Section particularly desire to urge small dealers and retail shopkeepers to take care when purchasing Genuine White and Red Lead to insist on its being marked and invoiced *as such*. This is necessary for their own protection, as in the event of the quality of the article sold by the retailer being challenged, he has only to produce his guarantee of quality, that is the marked keg or the invoice, and the dealer at once becomes responsible and liable to

prosecution should the article prove other than of the quality guaranteed. The Section issue this warning as they have no desire to harass the small retailer if the real offender is the firm from whom he buys. The Section will be glad to hear from such of our readers as are interested, that the action they have taken meets with their approval, and will always be pleased to answer any inquiries regarding the Merchandise Marks Act and its bearing on the White and Red Lead Trade.

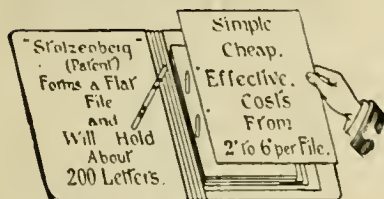
MEETINGS FOR THE WEEK.

- MONDAY, 18th.—Society of Arts, B. (Cantor Lectures). "Measurement of High Frequency Currents and Electric Waves," by Dr. J. A. Fleming, F.R.S.
WEDNESDAY, 20th.—Society of Arts, S. "The Aerograph Method of Distributing Colour," by Charles L. Burdick, Microscopical, S. "A 'Fero' Fructification from the Lower Coal Measures of Shor, Lancashire," by D. M. S. Watson. Exhibition of Balsam Mounted Slides by the late Andrew Pritchard.
THURSDAY, 21st.—Chemical, 8.30. "Relation of Position Isomerism to Optical Activity—Part V., Rotation of the Menthyl Esters of the Isomeric Dibromobenzoic Acids," by J. B. Cohen and I. H. Zortman. "Azo-derivatives from α -Naphtho-methyl-coumarin," by J. T. Hewitt and H. V. Mitchell. "Supposed Identity of Dihydroisaurulene and of Dihydro-isaurulene with 1:1-Dimethylhexahydrobenzene," by A. W. Crossley and N. Renouf. "Slow Combustion of Carbon Disulphide," by N. Smith.

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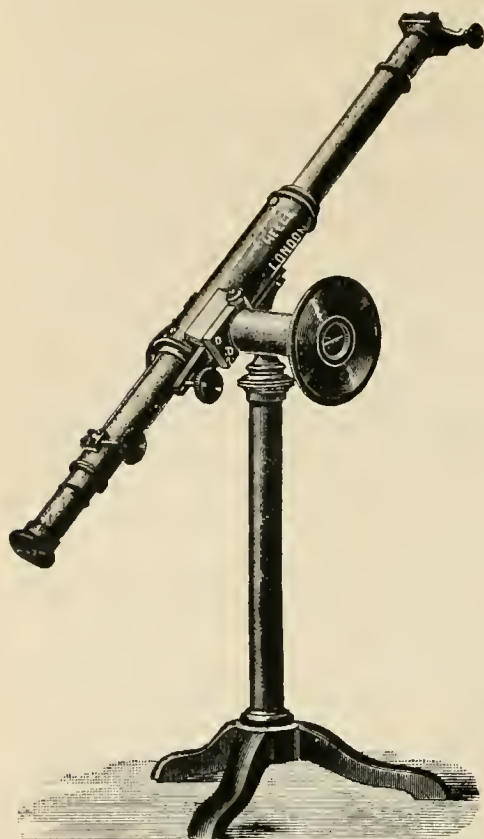
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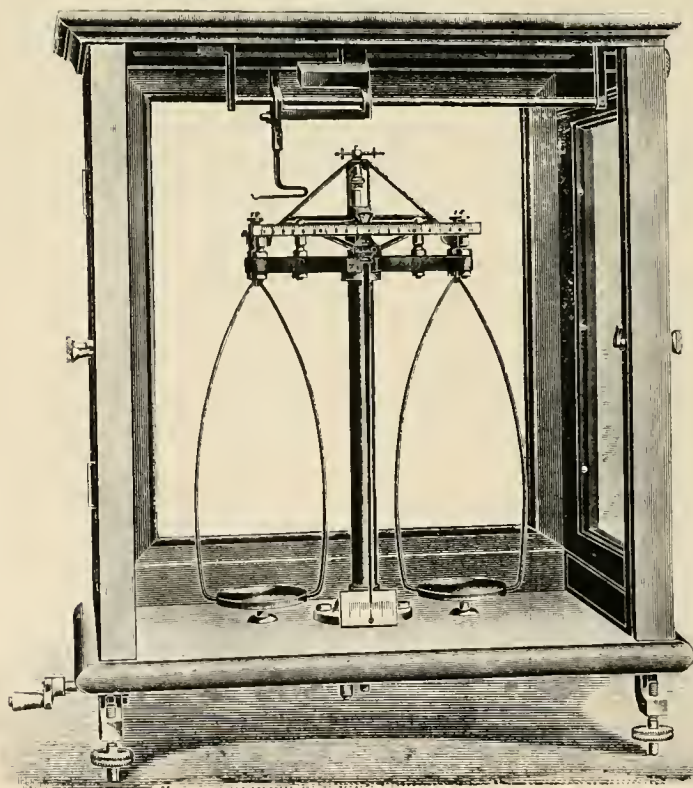
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THE CHEMICAL NEWS.

VOL. XCII., No. 2404.

NEW RESEARCHES ON THE ATOMIC WEIGHT OF NITROGEN.*

By PHILIPPE A GUYE

(Continued from p. 276).

II. *The Modern Physico-chemical Methods are sufficiently accurate for Determining exactly the Second Decimal of the Atomic Weight of Nitrogen.*

THE importance of these methods does not appear to have been properly understood so far by all chemists. The fault is perhaps due to physico-chemists, who have not sufficiently expressed their views in order to elicit from them cause and effect. I may be permitted, therefore, to speak of the first principles, seeking to establish their co-ordination, and to place in evidence their perfect harmony; for the details the short time at my disposal obliges me to refer to original memoirs. For the sake of clearness I am forced also to leave aside the historical aspect of the question, so as to present it only in the simplest form, such as is to-day derived from memoirs of the subject.

It is a well acknowledged fact that the rule of Avogadro-Ampère is only the expression of an approximate law; gases or vapours have coefficients of expansion, nearly identical, it is true, but at the same time sufficiently different to make it impossible to merge them into a common value. From the result of applying Avogadro-Ampère's rule to the determination of the molecular weights of gases, taking one of them—oxygen, for example—as the standard, one obtains for the same gas slightly different values, according to the conditions of temperature and pressure during the operation; in certain cases the divergence from the theoretical value exceeds 2 per cent. Example, sulphurous anhydride at 0° .

In other words, in order to utilise the densities of gases for the exact and rigorous determination of their molecular weights, and, consequently, the atomic weights of the elements of which they are composed, it is necessary to subject these densities to a correction depending on the conditions of temperature and pressure of the operation.

We are now in the position to fix the value of this correction by four different methods, utilising different experimental data, and—a fact really worthy of attention—these methods of correction may all be based upon the characteristic equation of Van der Waals, the relation which has proved so fruitful in science.

Van der Waals' equation, reduced to unit volume—

$$\left(p + \frac{a}{v^2}\right)(v-b) = (1+a)(1-b)(1+\sigma t) \quad (1).$$

furnishes the exact enunciation of Avogadro-Ampère's rule. From this it is deduced that at normal temperature and pressure the volumes of different gases containing exactly the same number of molecules are as the numbers—

$$\frac{1}{(1+a)(1-b)}, \frac{1}{(1+a')(1-b')}, \frac{1}{(1+a'')(1-b'')} \text{ \&c.,}$$

the constants $a, b, a', b', a'', b'', \text{ \&c.,}$ referring to the different gases in question.

These constants being much less than unity (for gases at 0° they are less than 0.01), the above numbers approximate to unity.

If L represent the weight of a normal litre of gas (i.e., at normal temperature and pressure, $h=0, \lambda=45^{\circ}$), there

will necessarily be between the molecular weight M and the weight L the relation—

$$M = \frac{RL}{(1+a)(1-b)} \quad (2);$$

R being a common constant for all the gases depending on the choice of units.

In the litre.-gram.-atm. system, and reducing the molecular weights to $O_2=32$, the most probable value of R is—

$$R = 22.412 \text{ litres.}$$

In order to fix the exact value of the molecular weight of a gas, of which the density at 0° has been determined, it is also necessary to know the numerical value of the product $(1+a)(1-b)$. Many methods lead to this result.

Method by Reduction of the Critical Elements to 0° and 1 Atmosphere.—What would first occur to one's mind would be to fix the numerical values of a and b by means of Van der Waals' equation. According to this scientist, the values of the coefficients a and b may be determined numerically, when the values of the critical constants of the gas are known, at the critical temperature T_c and critical pressure p_c .

But Van der Waals' equation is itself only an approximate formula, and experience has shown that the coefficients a and b of a gas, instead of remaining constant, vary in an appreciable manner with the temperature and pressure. It is only quite recently that these variations have been represented with a sufficient exactitude to satisfy rigorously the above relation (2). If the values of the coefficients a and b at normal temperature and pressure be represented by a_0 and b_0 , the formula giving the exact molecular weight becomes—

$$M = \frac{22.412 L}{(1+a_0)(1-b_0)} \quad (3).$$

Hence the name *method by reduction of the critical elements at 0° and 1 atmosphere* given to this process of calculation.

The calculation is most simply made by sub-dividing the gases into two groups, according as their critical temperature is inferior (permanent gases) or superior (liquefiable gases) at 0° . For permanent gases the relation (3) is replaced by the following:—

$$M = \frac{(22.412 + mT_c)L}{(1+a)(1-b)};$$

where $m=0.0000623$. This makes—

$$(1+a_0)(1-b_0) = (1+a)(1-b) - 0.00000210 T_c,$$

keeping to the general expression—

$$M = \frac{22.412 L}{(1+a_0)(1-b_0)}.$$

For liquefiable gases, relation (3) serves by calculating a_0 and b_0 from the formulæ—

$$a_0 = a \left(\frac{T_c}{T} \right)^2, \quad b = b \left(1 - \frac{T_c - T}{T_c} \right) (1 - \beta p_c);$$

where $\beta=0.0032229$.

In all these formulæ, a and b represent the constants of the equation reduced to unit-volume; these constants are calculated by means of the elements T_c and p_c obtained by experiment.

Without remaining longer over these details, it is interesting to note (Table V.) the results obtained with gases whose densities are the best known, making temporarily an approximation for nitrogen and gaseous compounds of nitrogen, since the atomic weight of this element is under discussion.

TABLE V.—Molecular Weights by Reduction of the Critical Elements.

O_2 (standard) ..	32	CO_2	44.003
H_2	2.0153	C_2H	26.018
Ar	39.866	HCl	36.484
CO	28.001	SO_2	64.065

* From the *Bulletin de la Société Chimique de Paris*, 1905.

A system of atomic weights is easily deduced from these numbers, which are thus determined by observations exclusively physico-chemical, and each by an independent method.

TABLE VI.—Atomic Weights.

Hydrogen, from H ₂	1.0077
Sulphur, from SO ₂	32.065
Carbon, from CO	12.001
" CO ₂	12.003
" C ₂ H ₂	12.002—Mean ..
Chlorine, from HCl	35.476
Argon, from Ar	39.866

The values of these same atomic weights, determined by the best acknowledged purely gravimetric methods, are—

H, 1.0076; C, 12.002; S, 32.058 to 32.074; Cl, 35.473

The agreement is certainly excellent; it will be remarked, in particular, the almost identical figures found for carbon, from the mean of the densities of the three gases CO, C₂H₂, CO₂ (Table VI.).

Method of Density-limits.—If A' represent the mean coefficient of divergence from Mariotte's law between the pressure $p_1 + 1$ atm., and the pressure infinitely reduced $p_0 = 0$ atm., and V₁ and V₀ the corresponding volumes of the gases at these pressures, we obtain without difficulty, from Van der Waals' equation, the following relation:—

$$1 - A' = \frac{1}{(1+a)(1-b)} \quad \dots (4).$$

For the fundamental relation above, the following might then be substituted:—

$$M = 22.312 L (1 - A') \quad \dots (5),$$

the latter serving to calculate the exact molecular weights.

We have just deduced it from the equation in which it is implicitly contained; it was announced for the first time in the form of a hypothesis, which may be stated thus:—

The rule of Avogadro-Ampère is a law-limit; it is rigidly true at zero-pressure.

This hypothesis seems to us to-day to follow from Van der Waals' formula, to which it seemed to me good to refer it, for it is always wise to reduce the number of hypotheses used in science.

This mode of action presents also another advantage to which we shall have occasion to return.

The application of the relation (5) requires the knowledge of the coefficient A'. Berthelot has shown that in what concerns the permanent gases this coefficient might be taken as equal to that found between 1 and 2 atmospheres. For liquefiable gases, the coefficient A' varies with the reduction of the pressure; the value found between 1 and 2 atmospheres cannot therefore be used directly—it must be subjected to a correction, the method of calculating which has been also pointed out by Berthelot.

It seems, however, that this correction is not yet altogether sufficient; it will certainly be improved upon finally; furthermore, the direct determination of the compressibility under pressures near zero presents experimentally three great difficulties; it may be asked whether these difficulties have been all surmounted by the beautiful researches of Ramsay and Steele on the density-limits of organic compounds in the gaseous state. In the meantime to avoid discussion I will only apply the method of density-limits to the permanent gases, and will endeavour to demonstrate the perfect agreement of these results with those of the preceding method.

If these two methods agree, we have the identity—

$$1 - A' = \frac{1}{(1+a)(1-b)},$$

which, considering the minuteness of the different terms of the unit, becomes—

$$A' = a - b = a - b - 0.00000210 T_c,$$

in the case of the permanent gases.

The data of Table VII. justify the correctness of this conclusion.

TABLE VII.

Gas	A' (Chappuis).	A' (Rayleigh).	A' (Jaquero and Scherer).	(a ₀ - b ₀) by the critical constants.
O ₂ ..	—	0.00094	0.00097	0.00095
H ₂ ..	-0.00058	-0.00053	-0.00052	-0.00052
CO ..	—	0.00081	—	0.00084
NO ..	—	—	0.00117	0.00104
N ₂ ..	0.00043	0.00056	—	0.00074
Ar ..	—	—	—	0.00090

It follows from these figures that the correction factor $1 - A'$ or—

$$\frac{1}{(1+a_0)(1-b_0)},$$

calculated by the two methods, agree within a few hundred thousandths—the divergence is greatest for nitric oxide and nitrogen; even in this case the divergence is only of the ten-thousandth order.

This shows that, with the same densities as those used for Table V., the method of density-limits (Formula 5) leads to practically the same values for molecular weights, and, consequently, to the same atomic weights as those placed in Table VI.

Method of the Corresponding Vapour Densities.—This method also depends upon a theorem formulated by Van der Waals in connection with the celebrated theory of corresponding states. The illustrious physicist has proved that, between the densities d_1 and d_2 of two gases, determined under corresponding conditions of temperature T_1 and T_2 , and of pressure p_1 and p_2 , there is the relation—

$$\frac{d_1}{d_2} = \frac{M_1}{M_2} \frac{p_{c1}}{p_{c2}} \frac{T_{c1}}{T_{c2}} \quad \dots (6);$$

M_1 and M_2 being the molecular weights of the two gases, T_{c1} , p_{c1} , and T_{c2} , p_{c2} their critical constants.

By reason of the conditions of correspondence this relation may be written—

$$\frac{d_1}{d_2} = \frac{M_1}{M_2} \frac{p_1}{p_2} \frac{T_2}{T_1}, \text{ or } \frac{d_1 T_1}{p_1} : \frac{d_2 T_2}{p_2} = \frac{M_1}{M_2} \quad \dots (7).$$

At a nearly constant factor $d_1 T_1 / p_1$ and $d_2 T_2 / p_2$ represent the vapour densities determined at T_1 and p_1 for the first gas, and at T_2 and p_2 for the second gas, then reduced to 0° and 1 atmosphere by the formulæ of perfect gases (Mariotte and Gay-Lussac's laws). Thence the fundamental theorem:—

The densities of gases, determined under corresponding conditions of temperature and pressure, reduced to 0° and 1 atmosphere by the formulæ of the perfect gases, are rigidly proportional to the molecular weights of these gases.

This theorem, which has only lately been demonstrated, was formulated some years ago by Leduc, as a result of his experimental researches on gases.

Properly speaking, its direct verification constitutes the method of corresponding vapour densities.

Unfortunately the elements of verification are not numerous. For want of direct determinations under corresponding conditions, the densities at 0° and 1 atmosphere may be used, when the coefficients of expansion and compressibility of the gases considered are accurately known, in order to reduce them to corresponding conditions of temperature and pressure.

I shall later have occasion to mention some verifications of this order; for the moment I will merely mention certain particularly interesting cases. The first concerns the molecular weight of argon; its critical constants coincide almost exactly with those of oxygen.

	T_c	p_c	L.
Oxygen	154.2	50.8	1.4290
Argon	152.0	50.6	1.7802

From this it follows that, at 0° and 1 atmosphere, the two gases are in corresponding conditions, the same as at all equal temperatures and pressures; the exact molecular weight of argon may therefore be deduced from the simple ratio of the densities, which gives—

$$\text{Ar} = 32 \cdot \frac{1.7802}{1.4290} = 39.865.$$

By the method of reduction of the critical elements we found (Tables V. and VI.)—

$$\text{Ar} = 39.866.$$

The agreement leaves nothing to be desired.

A second particular case is that in which the two gases compared are considered at the temperatures at which they rigidly follow Mariotte's law and Avogadro-Ampère's law. Berthelot has shown that this temperature is equal to $2.45 T_c$; for brevity, I will give it the name of *Avogadro's temperature*. In this case the application of the theorem relative to corresponding densities reduces itself to a very simple formula when the densities at 0° are known. Let t and t' be the temperatures (centigrade) of Avogadro for the two gases, a and a' their mean coefficients of expansion between 0° and t' and between 0° and T' at a pressure of 1 atmosphere, L and L' the weights of a normal litre of the two gases, M and M' their molecular weights. We have then evidently the relation—

$$M = M' \frac{L}{L'} \frac{1 + (t' - \gamma)t'}{1 + (a - \gamma)t} = M' \frac{L}{L'} [1 + (a' - \gamma)t' - (a - \gamma)t];$$

γ is the coefficient of the perfect gases, for which may be adopted the value proposed by Berthelot:—

$$\gamma = 0.00366195 \text{ or } 0.003662.$$

A third particular case is that in which these gases are considered at very high temperatures—for example, above 1000° for gases like oxygen and nitrogen. Computation shows that the variations from the laws of Mariotte and Avogadro-Ampère represent only a few units of the hundred-thousandth order; they are therefore negligible. If the gases are not dissociated at these temperatures, the direct ratio of the densities will give without correction the ratio of the exact molecular weights. Jaquerod and Perrot, experimenting with elements with reference to the determination of the melting-point of gold, found the number 14.008 for the density of nitrogen at 1067° , compared to that of oxygen taken as 16. We will return later to this result.

Method of Molecular Volumes.—The principle of corresponding densities has been verified by Leduc in the course of his remarkable researches on gases. The determination of densities at all temperatures—demanded for the direct verification of this principle—being very complicated, Leduc thought that the comparison would be more easily made by considering all gases at 0° , and by taking into account the volume occupied under these circumstances by a gram-molecule of the gas considered. This volume, ϕ , according to the theory of corresponding states, ought to be for all gases a certain function of T/T_c and of p/p_c . The researches of Leduc on the coefficients of the compressibility and expansion of gases, led him to determine numerically the constants of the formulæ which permit the calculation of ϕ when T_c and p_c are known. The explanation of these methods of calculation being, without doubt, known to you by the detailed studies of which they have been the object, I will confine myself to pointing out the fact that the system of atomic weights adopted by this observer to satisfy the relations indicated, correspond almost exactly with those deduced from the molecular weights obtained from the reduction of the critical elements at 0° or from the density limits. I reproduce them here:—

$$\text{H} = 1.0076, \text{C} = 12.004, \text{Cl} = 35.470, \text{S} = 32.056.$$

The Accuracy attainable for the Determination of Densities.—The preceding considerations show that the

correction factors resulting from the rigid application of the law of Avogadro-Ampère may be determined in several independent ways, and that the values thus obtained agree perfectly together within the limits of experimental error.

In order to judge of the accuracy obtainable by physico-chemical methods, it is advisable to know the degree of accuracy with which the densities of the gases may be determined. As latterly the means of carrying out these manipulations have been brought to greater perfection, I will confine myself to making mention of the values found for certain gases recently investigated by different observers.

TABLE VIII.—Weights of the normal Litre of certain Gases Determined by different Observers.

Gas.	Leduc.	Rayleigh.	Morley.	Lab. Guye.
O ₂ . .	1.4288	1.42905	1.4290	1.4292 (c)
H ₂ . .	0.08982	[0.08998] (a)	0.089873	—
N ₂ . .	1.2503	1.2507	—	—
CO . .	1.2501	1.2504	—	—
CO ₂ . .	1.9763	1.9769	—	1.9768 (d)
N ₂ O . .	1.9780	1.9777	—	1.9774 (d)
SO ₂ . .	2.9266	—	—	2.9266 (c)
Ar . .	—	1.7802	1.7801 (b)	—

(a) Lord Rayleigh has recognised (c) J. and P.
that this value is too high. (d) G. and P.

(b) Ramsay.

Taking into account the fact that the determinations were carried out in different places, often by different methods, nearly always on gases of different origin, we realise that the agreement is very satisfactory. The extreme range of variation is 1/4800 for O₂, 1/4200 for N₂ and CO, 1/3300 for CO₂ and N₂O. Under these conditions it may be admitted, without being too sanguine, that the mean values ought to be correct to 1/5000 at least, often even to 1/10,000. The correction factors used for calculating the exact molecular weights of gases often agree to nearly 1/10,000 when the value is fixed by different methods. The degree of accuracy obtained for the three physico-chemical determinations of the atomic weight of carbon, starting with the densities of CO, C₂H₂, and CO₂, with an extreme variation of 1/6000, is a confirmation of these deductions (Table VI.).

Returning to nitrogen, the exact determination of the second decimal of its atomic weight to within one unit gives only an exactitude of 1/1400; if an accuracy of 1/5000 be granted to the physico-chemical methods, the uncertainty of the atomic weight of nitrogen will only be ± 0.003 . It may therefore be logically concluded that the modern physico-chemical methods for the determination of the molecular weights of gases and of the atomic weights of their constituents are capable of sufficient accuracy to fix the exact value of the second decimal of the atomic weight of nitrogen.

(To be continued).

The Iron and Steel Institute.—The Council of the Iron and Steel Institute have arranged that the Annual General Meeting of the Institute shall be held in London on May 10th and 11th, 1906. In place of the usual Autumn Meeting a joint meeting with the American Institute of Mining Engineers will be held in London on July 23rd to 28th. It is intended during the week following to give the American visitors an opportunity of seeing some of the iron-making districts. It is anticipated that the visiting party will include many of the leading ironmasters who entertained the Iron and Steel Institute in America in 1890 and 1904. The Lord Mayor of London has kindly consented to act as Chairman of the London Reception Committee, and to give an evening Reception at the Mansion House.

THE PHYSICS OF ORE FLOTATION.*

By J. SWINBURNE and G. RUDORF, Ph.D., B.Sc.

ARGUMENT.—Theory that bells of sulphuretted hydrogen carry up the particles of sulphide is invalid. No hydrogen sulphide evolved. Adhesion between solid and liquid. Surface tension of liquid. Their joint action. Cohesion of liquids. Sometimes enormous. Air films and adhesion. Rise of temperature reduces surface tension, which becomes zero at critical-point. Rise of temperature reduces adhesion, probably to zero at boiling-point. Raising temperature to near boiling-point thus necessary for flotation. Effect of air films. Presence of carbonates necessary.

It often happens that an invention is made by a process which is in exact accord with the original meaning of the word; that is to say, it is come upon without the inventor necessarily understanding the nature of the underlying phenomena at the time. Scientific people generally arrive on the scene at a later date with explanations which may be right, but are sometimes wrong. We therefore bring forward an explanation for criticism which we think is correct, at present at any rate.

Concentration of sulphide ores by flotation was introduced by Potter in 1901, though concentration by means of oil had been already invented by Elmore. The Elmore process, however, is not a flotation process in the same sense, and therefore does not concern us for the present. Since Potter brought forward the idea of concentration by flotation other inventors have been at work in the same direction; so we will treat the subject rather broadly.

Concentration by flotation is carried out by treating the crushed ore with a suitable solution, such as a strong solution of acid sodium sulphate, at a suitable temperature, which is near the boiling-point of water. Part of the ore then rises to the top, and is skimmed off, or otherwise separated, and this forms the concentrate.

The explanation generally given is delightfully simple. It is said that the acid liberates hydrogen sulphide from the sulphides, and the gas then sticks to the particles and carries them up. As the acid does not act on the gangue, which in such cases is largely silicious material, the gangue is not carried up; and thus the separation takes place.

This theory does not fit the facts. In the first place, the sulphides generally treated are not attacked by the acid solution, so that there is no hydrogen sulphide evolved; or, at most, it is given off in very small quantities, which are out of all proportion to the amount of material floated. The sulphides of zinc, iron, and manganese alone are attacked at all by dilute acids. It cannot therefore be the hydrogen sulphide that carries up the particles of sulphide. On the other hand, there is a considerable evolution of gas, but it is carbon dioxide, and carbon dioxide is chiefly given off by the gangue, which generally contains calcite and other carbonates, the carbonates being mostly produced by the weathering of the sulphide particles. According to the theory just given, this action, contrary to what is actually found to be the case, ought to float up either the gangue as a whole, leaving the sulphides, or it should at least float up the carbonates. The next point is that in most cases flotation does not take place at all until the temperature approaches boiling-point.

It seems probable that the whole matter is mainly a question of capillarity, or rather of adhesion and surface tension effects, and although other theories have been put forward, we think that ours, besides being very simple, explains the facts best.

Consider first the capillary attraction of the solution, or the adhesion between the solid and the liquid. This phenomenon is a little difficult to examine with surface tension also coming into play. The commonest example is the case of a barometer whose tube has been well boiled, so that there is no air or other gas in the Torricellian

vacuum, only mercury vapour. If the barometer is held slanting, so that the mercury runs right up to the top, it may then be put into its vertical position, and the mercury will remain at the top. The liquid mercury is then actually under considerable tension, and in so far as it is above the barometrical height, the mercury is supported by its adhesion to the glass, which it cannot leave. This instance is particularly to the point, because it is often supposed that mercury has no adhesion to glass, which is a mistake. It also shows that mercury has considerable adhesion to itself, or, as it is usually called, cohesion. Liquids have in this sense astonishing tensile strengths—if such a term may be used. Water will stand a pull of 5 megadynes per square centimetre, or 5 atmospheres. Berthelot filled a clean tube nearly full of water, and sealed it up with a small air bubble. He then heated the water; and under the pressure it dissolved all the air, but on cooling the air did not again separate out; the water occupied the whole space. It must therefore have been under a pull in all directions great enough to increase the volume of the water; and this force was borne by the adhesion of the liquid to the internal surface of the glass, together with its own cohesion. This shows that under certain circumstances the force of adhesion between the water and glass may be very great.

Surface tension depends on the liquid itself. It is, of course, concerned with the surface of separation of a liquid and a gas; but we may treat it, to adopt the old idea, as if the surface of the liquid were always in tension like a stretched membrane, except that the tension remains the same whether the surface be increased or diminished. It is measured in dynes per centimetre, just as the tension of the membrane might be measured by making a cut a centimetre long and stitching it up, and measuring the forces on the thread necessary to keep the lips of the cut together.

If a rod is held vertically, partly in a liquid, the adhesion will tend to make the liquid run up the sides of the rod. This movement will be opposed by gravity on the one hand and surface tension on the other. Gravity, of course, tends to keep the surface of the liquid quite level, so that it meets the rod at right angles. Surface tension, considered by itself, tends to keep the surface of the liquid as small as possible, the volume, of course, remaining constant. Thus, if the adhesion, in spite of gravity, pulls the liquid some way up the sides of the rod, the surface of the liquid is increased, and the surface tension therefore tends to prevent its rise. If there were no adhesion the surface tension would not allow the surface of the liquid to remain level where it approaches the rod, but would round the corner so as to get the least possible surface. This tendency would be upset by gravity, so that a state of equilibrium would be reached in which the surface was by no means the least for the volume; but any further reduction would be prevented by the force of gravity, which would overcome the surface tension. If the rod, as imagined, has, to begin with, no adhesion for the liquid, the liquid has a curved surface, so that the rod stands in a sort of hole in the liquid, the hole having its top belled like a trumpet. If the rod has a little adhesion the liquid will stick to it up to a level somewhat below the surface, and the liquid will then leave the surface at an angle and begin to turn over from there. As the adhesion is increased the liquid touches the rod higher and higher, and leaves the surface at a greater angle, until the surface is level, and meets the rod at right angles. If the adhesion is still greater the liquid rises against the rod, the angle changing until the liquid surface meets the surface of the rod at an acute angle in the new direction. The angle between the surface of the solid and the liquid called the contact angle thus depends on the adhesion, the surface tension, and gravity. Whether it depends at all on the gas in which the whole is immersed we do not know. The surface tension has nothing to do with the solid, while the adhesion depends both on the solid and on the liquid.

It may be well at this stage to consider briefly the question from a mathematical point of view.

* A Paper read before the Faraday Society, December 12, 1905.

Two distinct capillary forces come into play when any solid is dipped into any liquid. These are, as mentioned above, the adhesion and the cohesion.

1. *Adhesion*, the attraction between the solid and the liquid particles, is measured by the contact angle θ . If $\theta = 0^\circ$, i.e., $\cos. \theta = 1$, the liquid is said to be completely wet the solid. If $\theta = 180^\circ$, i.e., $\cos. \theta = -1$, the liquid does not wet the solid at all. For values of θ between 0° and 180° , i.e., of $\cos. \theta$ between $+1$ and -1 , there is imperfect wetting.

2. *Cohesion*, the attraction between the liquid particles themselves, is measured by the surface tension T , or, according to Quincke, more correctly by T divided by the specific gravity of the liquid. "Greasy" substances are those for which the cohesion of the liquid is greater than the adhesion of the liquid to the solid. The state of perfect wetting, for which $\theta = 0$, is very difficult to obtain, and even when obtained is difficult to preserve. The angle θ gradually increases on allowing solid and liquid to stand, provided both are in contact with air or some other gas. *In vacuo* it remains more or less constant, depending on the state of perfection of the vacuum. The adhesion therefore gets less and the solid gets "greasier." For this reason it is necessary in determining surface tensions to have a continually formed clean surface, or as Greenmach expresses it, the surface must be *in statu nascendi*. In order to do this Greenmach employed Röntgen's double-funnel method.

Quincke assumed that the solid surface gets coated with a very thin film of gas. For wetted substances this film must be thinner than the sphere of action of the molecular forces (about 0.0005 m.m.) and its thickness affects the value of θ . If the thickness be more than 0.0005 m.m. the substance is getting "greasy," and the degree of "greasiness" increases with time, i.e., as the gas-film gets thicker. This idea seems to have been objected to by Voltmann, but Wüllner showed that his objections were not valid, and later Magie upheld Quincke's work, and showed that only in very special cases was $\theta = 0$. This question of the air-film will be discussed more in detail below.

We will now return to the main argument and consider the case of a particle of ore and a gas-bell. The surface tension of the liquid tends to make the surface of the liquid as small as possible consistently with its still containing the air. If the particle has no adhesion the surface of the liquid surrounding it must be considered as part of the surface which has surface tension, so that the surface will arrange itself in such a way as to be the least possible to include both the gas and the particle. If the particle is large in proportion to the gas bubble the surface will surround it, the gas filling up any inequalities and helping to allow the surface to take the spherical form. If the particle is small the result will be a gas bell with a particle nearly inside it. Imagine now the particle to be endowed with increasing adhesion. It will first attach itself to the liquid at one or more points, and the angle of contact will become more and more obtuse. As this takes place the particle gets more and more into the liquid and out of the gas-bell, until the gas-bell is sticking to one side of it. If the adhesion increases more and more the final stage is that the bell has become a sphere which just touches the particle at one point. The bell will then leave the particle. In any intermediate case, such, for instance, as a bell of gas "sticking" to the particle, the adhesion would tend to reduce the surface of the solid that is in contact with the gas, and thus to make the bell more nearly spherical. The surface tension, on the other hand, is tending to make the surface of the liquid, including that in contact with the solid, as small as possible, consistently with its containing the gas.

In order to make particles of ore float up it is therefore necessary to get adhering gas-bells, and to get these to "stick" the surface tension and adhesion must be properly related. The term "stick" is not, of course, really applicable. The particle does not stick to the air-bell. We are accustomed to think of an air-bell as if it were

something independent of the liquid, floating about in it, forgetting that its attachment to a solid is a question of capillarity and surface phenomena, but for simplicity we may talk of the bell sticking to the solid.

Most constituents of ores have too great adhesion for water or dilute acid to be easily floated. To make it possible to separate them, it is necessary either to diminish the adhesion or to increase the surface tension T of the liquid. If the particles are sufficiently small for bells to raise them, the only conditions necessary are that the bell should be formed, and that the adhesion and surface tension should be rightly proportioned. Surface tension alters with temperature. The surface tension of water at ordinary temperatures is about 75.5 dynes per centimetre, and it falls with rise of temperature, approximately according to the formula $T = T_0 - 0.152t$, until it reaches zero at the critical temperature. As far as surface tension is concerned, therefore, the higher the temperature the less chance of success. But the adhesion is a different question. The adhesion of solids and liquids has been very little studied. It varies very considerably in different substances. Those with least adherence are generally called "greasy." This is because grease has little adhesion with water. Thus such a body as stibnite, which has little adhesion, may well be described as greasy. We are so accustomed to grease as a substance with small adhesion that when we meet others we naturally think them greasy. Thus if a spoon shows little adhesion for water, you know at once that the tablemaid has not rendered it chemically clean, and the small adhesion is due to a thin film of grease. But the small adhesion of stibnite is not due to a film of organic matter. The strange thing is, however, that bodies like stibnite, which have small adhesion for water and thus resemble grease, have apparently a greater adhesion for grease, and can therefore be separated by oil according to Elmore's method. It may be, not that the stibnite and oil have great mutual adhesion, but that the surface tension of the water is the main factor in making the stibnite and oil stick together. There are in this case several factors to consider; the surface tension of the water; the surface tension of the oil; the mutual adhesion of the ore and the water; of the ore and oil, and of the water and oil; so that the question is more complicated.

(To be continued.)

Electrical Preparation of Colloidal Solutions of Selenium and Sulphur.—Erich Müller and Romuald Nowakowski.—Colloidal solutions of selenium have been prepared by the reduction of neutral very dilute solutions of selenium dioxide with the calculated quantity of sulphur dioxide; also both the solid and liquid hydrosols have been obtained by adding drops of a very dilute solution of hydrazine hydrate to a warm dilute aqueous solution of selenium dioxide. The hydrosol possesses a blue fluorescence in transmitted light. To prepare the hydrosol electrically a small quantity of selenium is fused on platinum-foil, so that only a part of the foil is covered, and the cathode thus made is immersed in pure water, while a platinum-wire is used for the anode. With a low voltage solutions are obtained, which, after filtering, appear yellowish red in transmitted light in thick layers, and dirty yellow in thinner layers, while they are a whitey-red yellow colour in incident light. They are exceedingly stable, but deposit red selenium after a time. They are completely precipitated by electrolytes. Although the precipitation by electrolytes is not easy to see, its occurrence is indicated by the fact that on filtration the solutions run through colourless. Besides elementary selenium some hydrogen selenide is also formed. If a piece of platinum-foil on which some sulphur has been fused is immersed in pure water and a potential of 220 volts maintained for an hour, a milk-white solution of colloidal sulphur is formed, which smells strongly of sulphuretted hydrogen.

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PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 7th, 1905.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

MR. T. W. FIRTH CLARK was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. George Ernest Banner, Brooklyn, Highfield Road, Rock Ferry, Cheshire; Arthur Ernest Barker, B.A., B.Sc., 3, York Road, Chorlton-cum-Hardy; Charles Frederick Polwhele Bletchley, B.A., Downside College, Bath; Arthur Forbes Braid, Rose Mount, Dumbreck, Glasgow; William Caldwell, M.A., Mont-Cecil, Bloomfield, Belfast; Reginald William Lane Clarke, 15, Torridon Road, Hither Green, S.E.; William Boulton Conyngnam, "Sandon," Ballsbridge, Co. Dublin; Frederick Watkins Evans, 3, Charlotte Street, Hull; Hans Eduard Fierz, Ph.D., Clydach-on-Tawe, Glamorg., Wales; William Henry Matthews Jones, Leyden Villa, Chester; George Frederick Wesley Martin, 14, Castle Park, Lancaster; John Edmund Pitman, B.Sc., Hartley University College, Southampton; Harold Rogerson, M.Sc., 46, Bloomsbury Street, Bedford Square, W.C.; Frank Smith, B.Sc., 407, Church Road, Smithills, Bolton; Percy Charles Thornton, 9, Cantwell Road, Plumstead, S.E.; Ronald William Tonkin, 37, Oakill Road, Putney, S.W.; Elkan Wechsler, Ph.D., 59, Petherton Road, Canonbury, N.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Adam Lawson Kelly Adam; C. Chester Ahlum; James Edward Alcock; James Albert Allison; Charles Anthony, jun.; George Henry Barbrook; Marmaduke Barrowcliff; John Coggin Browne, B.Sc.; Bryce Chudleigh Burt, B.Sc.; Joseph Edward Coates, B.Sc.; Douglas Henry Bellars Cowman; Arthur Augustine Dallman; Joseph Morgan Davey; John Llewelyn Davies, B.A.; John Doull; Harry Dunlop; John Beaconsfield Gall; Sydney Montague Haig; Alfred Hart, M.A., B.Sc.; Jack Vernon Johnson Hayman; John Michael Higgins; William Basil Hill; Isaac Berkwood Hobsbaum; Cecil Hollins; Maurice Brooks Jack; Edward Towyn Jones, B.Sc.; Herbert Drake Law, B.Sc.; Rudolph Lyon; William McCleary; Robert Drysdale MacKechnie; Harry Martin; Harry George Fletcher Nicklewright, B.A.; John Dunlop Millen; Edalji Manekji Modi; Eric Haydn-Morris; John Motion; Henry Allen Dugdale Neville, B.Sc.; Francis Richard Penn; Hugh Donald Perkins; Percy Barker Phipson; Frederick John Pooler, B.Sc.; Thomas Rigby; James Frederick Fothergill Rowland, B.A.; Henry Rowley; Harold Marmion Royle; Arthur Gough Ruston, B.A., B.Sc.; Harry Nestor-Schnurmman; Douglas Temple Setterington; John Booty Tillot; Frank Tutin; George Stanley Walpole, B.Sc.; John Ledger White, D.Sc.; Gerard William Williams, B.A.

Of the following papers, those marked * were read:—

*202. "The Constitution of Nitrites. Part I. Two Varieties of Silver Nitrite." By PRAFULLA CHANDRA RAY and ATUL CHANDRA GANGULI.

It has generally been maintained that silver nitrite has a nitronic or non-oxylic constitution (Divers, *Trans.*, 1883, xliii., 455; 1885, xlvii., 205), but Emerson Reynolds seems, however, to be of opinion that "isomeric metallic nitrites of both the types (oxylic and imidic) exist which are also tautomeric in a marked degree" (*Trans.*, 1903, lxxxiii., 643).

The close analogy between mercurous nitrite and the corresponding silver compound has all along been pointed out in some of the authors' previous memoirs, and it would appear that under the action of heat the former behaves as

if it had a twofold constitution, as indicated by $\text{Hg}\cdot\text{NO}_2$ and $\text{Hg}\cdot\text{O}\cdot\text{NO}$ respectively (*Trans.*, 1903, lxxxiii., 491).

In the present communication, the authors hope to establish that silver nitrite also has this dual character, the two varieties being now described under the designation of α - and β -compounds respectively.

The α -Variety of Silver Nitrite.—This is the substance prepared by double decomposition between solutions of silver nitrate and sodium nitrite. The precipitate, consisting of a mealy crystalline powder, is drained at the pump, thoroughly washed with cold water, and dried under diminished pressure over sulphuric acid. The method of experiment was exactly the same as already described (*Trans.*, 1905, lxxxvii., 180). In the experiment of Divers and Shimidzu, after the apparatus had been exhausted the flow of mercury in the fall tube was stopped so as to allow the nitrous fumes evolved during the heating of the salt to act on the metallic silver set free, thereby favouring the formation of silver nitrate and nitric oxide (*Trans.*, 1885, xlvii., 634). In the present instance, the reverse method was followed. The rate of the flow of mercury was increased during the operation. By this arrangement the nitrous fumes were swept out of the tube almost as fast as they were generated, thus giving them much less chance of coming into contact with the silver. Moreover, these being absorbed by the caustic potash in the spiral, not only was the "soiling" of mercury in the Sprengel pump guarded against, but also the formation of nitric oxide by the secondary reaction between mercury and nitrous fumes prevented.

As it was desirable that the heating should be effected at a definite temperature, an asbestos box was made fitted up with mica windows; when the bath had reached the required temperature, the portion of the glass tube containing the substance was introduced into it through an opening. The various stages in the decomposition could also be easily watched through the mica plates.

The salt, when heated at temperatures ranging between 220° and 250° , fused, evolving red fumes. The gas which was collected in the reservoir of the pump was completely absorbed by a solution of ferrous sulphate, thus proving it to be nitric oxide. The residue solidified into a hard lump, consisting of a mixture of metallic silver and its nitrate. So far as this experiment goes, Divers' results are confirmed. The silver nitrite breaks up according to the equation $2\text{Ag}\cdot\text{NO}_2 = 2\text{Ag} + \text{N}_2\text{O}_4$ (1); at the same time, a portion of the silver thus set free acts upon the nitrous fumes, giving rise to silver nitrate and nitric oxide $\text{Ag} + \text{NO}(\text{NO}_2) = \text{AgNO}_3 + \text{NO}$ (2).

The β -Variety of Silver Nitrite.—The silver nitrite as prepared above is dissolved in boiling water, and from the hot saturated solution the nitrite is allowed to crystallise; when the mother-liquor becomes lukewarm, it is decanted into a shallow evaporating dish. When left over-night, slender needles are formed, which are drained and dried as above.

The heating was effected at exactly the same temperatures as in the preceding experiment, namely, between 200° and 250° . Very slight red fumes were noticed, and the substance did not fuse. The gas collected was not absorbed or coloured by a solution of ferrous sulphate, but was completely absorbed by a solution of alkaline pyrogallate, thus proving to be oxygen. As the salt did not fuse, the filamentous character of the original crystals was kept intact; the residue, on treatment with hot water, did not give the faintest opalescence with hydrochloric acid, and, when struck with a hammer, it solidified into a shining regulus of metallic silver.

The results are noteworthy in more respects than one. In the present instance, any formation of silver nitrate is out of the question. This salt is a stable compound, and it decomposes only slightly even at 444° (Divers, *Trans.*, 1899, lxxv., 83). It cannot therefore be urged that a little silver nitrate is at first formed, which breaks up and yields oxygen according to the equation $2\text{AgNO}_3 = 2\text{Ag} + \text{N}_2\text{O}_4 + \text{O}_2$.

The oxylic constitution of silver nitrite, however, offers

an easy explanation. Under the action of heat, the scission takes place as indicated by the dotted lines : $\text{Ag}-\text{O}-\text{NO}$.

Thus, from every two molecules of silver nitrite two molecules of nitric oxide and one molecule of oxygen are simultaneously set free. Now, although a mixture of these two gases in this proportion probably gives rise ordinarily to the peroxide, when it is rapidly drawn through or shaken up with a solution of caustic potash, the whole of the oxygen is not fixed, and a portion of it escapes uncombined. In short, the success of Gay-Lussac's method of preparing potassium nitrite is based on this fact (*Trans.*, 1899, lxxv., 85).

It is also remarkable that although a slight quantity of nitrous fumes was noticed, not a trace of silver nitrate was formed under the conditions present. Some dozen experiments were performed with samples of silver nitrite from separate preparations confirming the above results. We give below the result of one typical experiment.

0.43 grm. of salt gave 0.3 grm. of silver and 35.2 c.c. of moist nitrogen (extracted from the alkali in the spiral) at 32.5° and 754 m.m. Found $\text{Ag} = 69.76$, $\text{N} = 8.70$; calculated $\text{Ag} = 70.13$, $\text{N} = 9.09$ per cent.

(The percentages of nitrogen and silver found are rather low, but it should be remembered that the crystals, from the method of preparation, necessarily contained a trace of included mother-liquor).

The ratio of nitric to nitrogen was as 5:3.8. The oxygen collected was 2.6 c.c. at the above temperature and pressure.

(If the whole of the oxygen were absorbed, the alkali, on examination, would have yielded nitric and nitric nitrogen in equal quantities. A few experiments with lead nitrate under conditions exactly similar to the above were made, the only difference being that the substance was heated to a much higher temperature. The mean of three experiments gave the percentage of nitrogen as nitrate = 4.21, as nitrite = 4.21, whilst the percentage of oxygen was 4.6. According to the equation $\text{Pb}(\text{NO}_3)_2 = \text{PbO} + 2\text{NO}_2 + \text{O}$, these proportions should be $\text{N} = 8.48$ and $\text{O} = 4.84$. Hence it is clearly established that nitric peroxide, even when mixed with oxygen, in reacting on an alkali, yields the nitrate and nitrite in equal amount, the oxygen passing off unabsorbed. A trace of a higher oxide of lead which is found in the intermediate stage in the residue appears from its colour to be red lead (compare Divers, *Trans.*, 1899, lxxv., 84). These experiments also prove the trustworthiness of the method employed).

In conclusion, the authors wish it to be distinctly understood that a sharp line of demarcation cannot always be laid down between the fusible and the infusible varieties. As a result of experience gained during the course of several dozens of preparations, it has been found that even under exactly similar conditions the α -variety often turns out to be largely admixed with the β -variety; but the evidence of the formation of the latter in the pure state has been unmistakable.

It is to be hoped that further light will be thrown on the constitution of silver nitrite by the determination of specific gravity, as also by interaction with ethyl iodide.

*203. "The Products of Heating Silver Nitrite." By EDWARD DIVERS.

One of the purposes of this paper is to show that Rây and Gaṅguli, in the course of their interesting work on the effects of heating silver nitrite, have met with nothing which supports the belief that there are two chemical varieties of that salt. The other purpose of the paper is to endeavour to increase the confidence in the accuracy of their important experimental results, which are hardly in accordance with current views concerning the oxides of nitrogen.

Accounts of experiments on the effects of heating silver nitrite already published will be found in the following publications (*Trans.*, 1871, xxiv., 85; *Proc. Roy. Soc.*,

1871, xix., 429; and *Trans.*, 1885, xlvii., 634; and 1899, lxxv., 111). Precipitated and washed silver nitrite seems always to give some nitrate when heated, but, according to Rây and Gaṅguli, fractional re-crystallisation of the precipitated salt, effected by dissolving it in hot water and slowly cooling, gives as the last fraction crystals which may be so heated as to decompose without yielding any nitrate at all. The term fractional crystallisation is here used as appropriate, because the authors state that the salt before re-crystallising often behaves as though it were a mixture of its two forms, that which does not give nitrate and that which does, although on what grounds it is difficult to understand. They seem to have made no inspection of the precipitated salt under the lens, in order to seek for two forms of crystals. No distinction can be made as regards any essential difference between "a mealy crystalline powder" and "slender needles," since the former is only the result of hasty crystallisation during precipitation, and the latter are only obtained by slow crystallisation. The former variety of the salt, we are told, fused when heated at 220 and above; the latter variety did not in the least fuse. This statement cannot, however, be accepted as evidence, since silver nitrite does not fuse, but decomposes freely at about 180°, and will do so quickly and completely at that temperature without any fusion of its products of decomposition taking place. What does fuse in the decomposition of silver nitrite at 220—250° is any silver nitrate produced, this salt melting below 217°.

The remaining difference observed in the nature of the decomposition products of the two forms of silver nitrite supplies, however, no grounds whatever for stating, as Rây and Gaṅguli have done, that the essential or primary decomposition is into silver and nitric peroxide, in the one case, and into silver, nitric oxide, and oxygen in the other, since in this instance the one volume of oxygen and the two of nitric oxide will soon become nitric peroxide also. All that these authors can look to as marking the distinction which they believe to exist, is that they get, exclusive of products common to the two cases, some nitrate and some residual nitric oxide in the one case, whilst in the other, under the same conditions of procedure, they get paler gases, and can isolate from them a little oxygen.

There is not much difficulty in finding a sufficient reason for this difference of behaviour in the different way in which the salt will pack itself in the tube in the two cases. When the salt is heated in the state of powder, the resulting gases will be temporarily imprisoned in the interstices of the mass and the heat will penetrate it slowly enough to permit of the metallic silver of the already decomposed part being acted on by the gases evolved from the still decomposing parts of the nitrite. In this way nitrate will be formed and the gases made to contain a greater proportion of nitric oxide than would otherwise be the case. If, too, it be assumed that the gases are primarily oxygen and nitric oxide, their detention in the residual mass will give time for their union, more or less, into nitric peroxide, and thus account for the redder colour of the resulting gases. On the other hand, when the nitrite is in the form of slender needles, the slight contact of the needles with each other and with the walls of the tube, together with their open arrangement in the tube, will cause the whole mass of the salt to be decomposed so quickly and so nearly simultaneously by the heat suddenly radiated on it from the walls of the heating chamber employed, that, with the vacuum maintained, there will be no temporary detention of the gases by the solids, and no time, therefore, for secondary actions to take place. Not even the production of much nitric peroxide by the union of the oxygen with the lower oxide of nitrogen should be possible before the gases have reached the potassium hydroxide solution.

Rây and Gaṅguli attempt to strengthen their position that there are two constitutionally different silver nitrites by claiming that, in conjunction with Sen, one of them has shown already (*Trans.*, 1903, lxxiii., 491) that the decomposition of mercurous nitrite by heat indicates that

being greatly influenced by the solvent used. When ethyl alcohol is employed as the solvent, the reaction becomes unimolecular, and the velocity constant is approximately proportional to the change of temperature. The velocity constants of the reactions between the carbimide and fourteen alcohols are compared.

*207. "The Liberation of Tyrosine during Tryptic Proteolysis." (A Preliminary Communication). By ADRIAN JOHN BROWN and EDMUND THEODORE MILLAR.

A method of directly estimating tyrosine by bromination recently described by James H. Millar (*Trans. Guinness Research Laboratory*, 1903, vol. i., Part I.) appeared likely to furnish a means of measuring the activity of proteolytic change in those cases in which tyrosine is liberated during the breaking down of the protein molecule. An investigation in this direction was therefore commenced by the authors and the following is a summary of the results so far obtained.

1. J. H. Millar's method of estimating tyrosine by bromination is applicable to the estimation of tyrosine in the presence of proteins and their earlier cleavage products due to enzyme action if suitable control experiments are employed.

2. Tyrosine is not a late product of tryptic proteolysis, as is usually supposed; on the contrary, the tyrosine nucleus of a protein is attacked, and the whole of the tyrosine liberated during the first stage of tryptic digestion.

3. The resistance of the protein tyrosine nucleus to peptic hydrolysis is confirmed.

4. Attention is called to the similarity of Emil Fischer and E. Abderhalden's recent observations on the actions of tryptic and peptic enzymes on polypeptides containing a tyrosine nucleus (*Zeit. Physiol. Chem.*, 1905, xlv., 52) to the authors' observations on the actions of the same enzymes on proteins containing a tyrosine nucleus.

5. The authors' investigations appear to indicate a trustworthy means of differentiating enzymes of a peptic from those of a tryptic nature, and may assist in throwing some light on the confused state of knowledge with regard to the existence of a tyrosine nucleus in the different albumoses resulting from peptic and tryptic proteolysis.

208. "Ethyl Piperonylacetate." By WILLIAM HENRY PERKIN, Jun., and ROBERT ROBINSON.

When piperonylic acid, $\text{CH}_2\text{O}_2\text{:C}_6\text{H}_3\text{:CO}_2\text{H}$, is treated with phosphorus pentachloride, it is converted into piperonyl chloride, $\text{CH}_2\text{O}_2\text{:C}_6\text{H}_3\text{:COCl}$, a colourless, crystalline substance which melts at 80° and distils at 155° (25 m.m.). This acid chloride (1 mol.) reacts with the sodium derivative of ethyl acetoacetate (2 mols.) yielding the pale yellow crystalline sodium derivative of ethyl piperonyl-acetoacetate, $\text{CH}_2\text{O}_2\text{:C}_6\text{H}_3\text{:COCNa(CH}_3\text{:CO)_2CO}_2\text{Et}$; the corresponding eupric derivative, $(\text{C}_{14}\text{H}_{13}\text{O}_6)_2\text{Cu}$, crystallises from toluene in bluish-green plates. Ethyl piperonyl-acetoacetate, obtained from the pure sodium derivative by treatment with acids, is a colourless syrup which is soluble in sodium carbonate and gives a reddish-violet colouration with alcoholic ferric chloride.

When the sodium derivative is treated with ammonia and ammonium chloride (Claisen, *Annalen*, 1896, cclxc., 70), it is decomposed with formation of ethyl piperonylacetate, $\text{CH}_2\text{O}_2\text{:C}_6\text{H}_3\text{:CO-CH}_2\text{:CO}_2\text{Et}$, a solid, crystalline substance which melts at 41° , gives a reddish-violet colouration with ferric chloride, and yields a copper derivative, $(\text{C}_{12}\text{H}_{11}\text{O}_5)_2\text{Cu}$.

The authors wish to reserve, for a short time, the investigation of these new compounds.

(To be continued).

INSTITUTE OF CHEMISTRY DINNER.

THE Dinner of the Fellows and Associates of the Institute of Chemistry, was held at the Whitehall Rooms, Hotel Metropole, on Monday, the 11th inst., the President, Mr. DAVID HOWARD, in the Chair.

Owing to the dense fog which prevailed, a number of distinguished guests, including Lord Reay, Mr. Justice Buckley, Mr. Justice Swinfen Eady, Professor Meldola (President of the Chemical Society), and Sir R. Douglas Powell, Bart. (President of the Royal College of Physicians), were unable to attend.

Those present included: Sir Thos. H. Elliott, Secretary of the Board of Agriculture; Sir Henry W. Primrose, Chairman of the Board of Inland Revenue; Sir Thos. Pittar, Chairman of the Customs Establishment; Sir William Ramsay, Sir Thos. Stevenson, Sir A. R. Binnie, President of the Institution of Civil Engineers; General J. H. Jeffcoat, Master of the Society of Apothecaries; Mr. John Tweedy, President of the Royal College of Surgeons; Mr. J. Gavey, President of the Institution of Electrical Engineers; Dr. Edward Divers, President of the Society of Chemical Industry; Mr. Edward J. Bevan, President of the Society of Public Analysts; Mr. R. A. Robinson, President of the Pharmaceutical Society of Great Britain; Professor W. A. Tilden, Professor J. Millar Thomson, Sir W. H. Bell, Mr. H. H. Cunyngame, Assistant Under-Secretary of State, Home Office; Mr. W. R. Bousfield, K.C., M.P., Mr. J. M. Astbury, K.C., Mr. A. Gordon Salamon, Hon. Treasurer; Dr. F. Gowland Hopkins, Dr. J. A. Voelcker, Lieut.-Colonel Charles E. Cassal, Dr. W. Kellner, Mr. C. E. Groves, Mr. T. Fairley, Mr. W. W. Fisher, Mr. George Beilby, Mr. Bertram Blount, Mr. Otto Hehner, and Mr. Richard B. Pilcher, Registrar and Secretary.

The loyal toasts having been honoured, Professor J. MILLAR THOMSON proposed "The Houses of Parliament," and alluded to the employment of professional chemists by the various departments of State. In responding, Mr. Bousfield, K.C., M.P., said that, although the Government had done much to foster technical education, there was still much to be done in the promotion of research. We had advanced a good deal in our ideas of what the State should do for science, but not enough so far as the higher walks of it are concerned.

Mr. R. A. ROBINSON, in proposing "The Institute of Chemistry of Great Britain and Ireland," said that it was a great pleasure to him as President of the Pharmaceutical Society of Great Britain to have an opportunity of congratulating the Institute on having attained its present important position. The Institute had nearly 1200 Fellows and Associates, and was doing an important public work in carrying out the objects of its charter, namely, "To promote the better education of persons desirous of becoming public and technical analysts and chemical advisers on scientific subjects; to examine candidates and to grant certificates of competency; and to elevate the profession of Consulting and Analytical Chemistry by setting up a high standard of scientific and practical proficiency, and by insisting on the observance of strict rules in regard to professional conduct." As an instance of the success it had attained in promoting these objects, he mentioned that 93 per cent of the Public Analysts under the Sale of Food and Drugs Acts were Fellows of the Institute.

THE PRESIDENT, in reply, said that he had been intimately connected with the Institute from its foundation in 1877. They started with a very high ideal. They wished to raise the status of the professional chemist to something like the level of other learned professions. To-day, the position of the professional chemist was higher in England than elsewhere, because there was more independence of thought, and that individual excellence and individual devotion to duty which was required in a true professional spirit. He viewed with great apprehension the increasing desire for cheapness. It was quite true that you could get

Royal Institution.—On Thursday next, December 28, at 3 o'clock, Professor H. H. Turner will deliver the first of the Christmas Course of Six Illustrated Lectures, adapted to a juvenile auditory, on "Astronomy."

work done cheaper wholesale than retail, but it was not in the mass that they got the intelligent progress that was wanted. He earnestly hoped that the temptation to cheapness would not be allowed to enter professional scientific questions. The examinations of the Institute were attended now by over 100 Candidates yearly, and arrangements were being made for the conduct of examinations in the Colonies. He also alluded to the new scheme of Examinations in Technical Chemistry which the Institute will put into operation next year.

Sir THOMAS STEVENSON proposed the toast of "The Learned Societies and Institutions," which was acknowledged by Mr. TWEEDY and Sir A. R. BINNIE.

Sir WILLIAM RAMSAY proposed "The Guests." Sir THOMAS H. ELLIOTT and Mr. ASTBURY responded, and the proceedings terminated.

FARADAY SOCIETY.

Ordinary Meeting, October 31st, 1905.

Lord KELVIN, President, in the Chair.

PROF. ERNEST WILSON, gave a *résumé* of his paper on "Alternate Current Electrolysis," which had been taken as read at the previous meeting. (See CHEMICAL NEWS, vol. xcii., p. 198).

Mr. W. R. COOPER then read an abstract of his paper on "Alternate Current Electrolysis as shown by Oscillograph Records," illustrating his remarks by projecting on the screen a selection of his photographic records.

It is pointed out that although polarisation is of the nature of capacity in an alternate current circuit, there is a considerable difference. What might be termed the E.M.F. of a condenser rises and falls as rapidly as the applied pressure, but although the E.M.F. of polarisation may rise as rapidly as the applied pressure, it falls more slowly, with the result that, under suitable conditions, the current curve may depart very considerably from the sine form. Actual oscillograph records are reproduced in support of this view. In considering the subject it has been very generally assumed that the current follows a sine curve. Since the curve obtained depends very much on the conditions of the experiment, it is necessary to define the conditions very carefully before conclusions can be drawn from different experiments. Oscillograph records of electrolytic rectification were also shown.

Mr. A. E. TROTTER referred to the bearing of work on alternate current electrolysis on the corrosion of water and gas pipes caused by stray currents from alternate current systems. He described some practical experiments he had made with lead pipes buried in the earth; these experiments showed that there was a minimum current density or a minimum voltage—he was not sure which—below which no corrosion took place. More work was required to be done in order to indicate the exact conditions necessary for corrosion, but great caution was necessary in the application of scientific experiments to practice.

Mr. J. SWINBURNE thought that the greater absorption of energy found by Professor Wilson at the lower frequencies was simply due to diffusion, and this was borne out by Mr. Cooper's curves.

Dr. F. MOLLWO PERKIN said he had found that platinum plates electrolysed alternately in dilute sulphuric acid were more corroded at low than at high frequencies; a colloidal solution of platinum seemed to form, and the electrodes had an etched appearance.

Professor A. K. HUNTINGTON contributed a "Note on the Crystalline Structure of Electro-deposited Copper," which was illustrated by photomicrographs of sections of the deposits referred to in the paper.

In Mr. Cowper-Coles's process for making copper-wire electrolytically, a spiral scratch or groove on the mandril causes the copper deposited on it to part so easily that a long ribbon can be obtained. The author's explanation is

that the direction of the lines of crystallisation of an electro-deposited metal are the same as in a casting made on surfaces having the same inclination, i.e., the crystals form at right angles to the surface on which the deposit or the casting is made. It follows that when the crystals which form on surfaces more or less at an angle to one another meet, there will be want of continuity in the two sets of crystals, and a line of weakness will be developed. Therefore in castings and deposits when strength and not rupture is aimed at, it is important to avoid sharp angles. In the case of a cathode plate which has been deposited on a thin strip of electro-deposited copper, the crystals of the original strip continued in some cases in the cathode plate. On annealing the electro-deposited copper the long crystals of the deposit are completely broken up and become largely twinned. Hence brittleness due to the direction in which crystals form in castings and electro-deposits may be modified and probably completely removed by suitable annealing, unless the continuity is entirely broken.

Mr. J. F. R. RHODIN thought that structure of the copper deposited in a groove, such as Mr. Cowper-Coles employed, depended on electrostatic repulsion rather than on crystalline form. The fringing at the edge of a deposit, even where the current density was not high, seemed to him to him to confirm that explanation.

Mr. W. POLLARD DIGBY's paper on "Some Observations respecting the Relation of Stability to Electro-chemical Efficiency in Hypochlorite Production" was taken as read.

The author commenced by drawing attention to the fact that in all electrolytic methods of producing hypochlorite solutions, only a small portion, rarely more than 18 per cent of the chlorine usually present in the form of chloride, is converted into hypochlorite, and suggests that the amount of available chlorine produced from a sodium chloride solution depends upon the relation which the amount of unconverted sodium chloride actually present between the electrodes bears to the current density. As regards stability, particulars are given of two tests in which the rate of depreciation, although only 0.3 to 0.4 grm. in twelve hours per litre for solutions containing 8 grms. of available chlorine per litre, caused a very great depreciation in the yield per kilowatt hour supplied. The suggestion is advanced that no test of the efficiency of any apparatus for the electrolytic production of the hypochlorites can be regarded as complete without an estimation of the losses through instability, and a mention of the volume of the contents of the electrolysis tank. While stability of solution does not greatly affect the efficiency of any continuous type of apparatus (in which the sodium chloride is fed in at one end and drawn off at the other end ready for continuous use), it will materially affect the efficiency in any non-continuous apparatus, or in any apparatus in which the electrolyte is circulated through an external cooling tank and returned to the electrolyser to be further worked up. It is suggested that the presence of minute quantities of iron in the solution have also a bearing on the depreciation.

MEETINGS FOR THE WEEK.

THURSDAY, 28th. } Royal Institution, 3. (Christmas Lectures,
SATURDAY, 30th. } adapted to a Juvenile Auditory). "Astronomy,"
by Prof. Herbert Hal Turner, D.Sc., F.R.S.

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THE CHEMICAL NEWS.

VOL. XCII., No. 2405.

ETCHING WITH HYDROFLUORIC ACID.

By NICHOLAS KNIGHT.

IN the interesting and practical experiment of etching on glass with fluor-spar and sulphuric acid, it is desirable to have both the surfaces of the glass coated with a thin layer of wax or paraffin; otherwise the upper surface becomes etched by the acid fumes, and the experiment is thereby marred. To obtain the desired effect, the writer for a number of years has kept an ordinary copper water-bath, 6 inches in diameter, nearly filled with paraffin. This is carefully heated to avoid burning until it is all melted. The glass object upon which the etching is to be made is immersed in this liquid and quickly withdrawn, when both sides and the ends as well are covered uniformly with a thin layer. After the etching is accomplished, the paraffin is easily removed by immersing the glass in warm water, not sufficiently hot to break it. The usual way of spreading the paraffin on one side of the glass by warming it with a small flame underneath often fractures the glass, but by the method described in the foregoing the etching is so easily and satisfactorily made that the students are eager to repeat the experiment, and they etch beautiful monograms and designs on various objects—watch-crystals, drinking-glasses, paper-weights, and similar articles. In this way there is a perpetual reminder of the days spent in the fascinating realms of experimental chemistry.

Cornell College, November 28, 1905.

THE PHYSICS OF ORE FLOTATION.*

By J. SWINBURNE and G. RUDORF, Ph.D., B.Sc.

(Concluded from p. 289).

RETURNING to the ores, the various sulphides have different adhesions. The gangue, as a rule, has very great adhesion, and cannot be floated. Even such bodies as stibnite, unless very finely ground, have too much adhesion to be floated at ordinary temperatures. The adhesion is altered enormously with change of temperature, however. This is well known in the case of taking out spots of grease from clothes. If the cloth is ironed with blotting-paper underneath it, the grease will run from the hot cloth into the cooler blotting-paper. In the same way, cloth that seems dry when cooled seems damper when warmed, as the adhesion or capillary attraction is reduced. A thick piece of dry bread when toasted gets quite moist in the centre, partly because the water has moved in from the outside, which is hotter than the inside, and partly because the adhesion is less. In the case of ores, many of the sulphides, such as galena, stibnite, and molybdenite, have their adhesion reduced enough to be floated easily near the temperature of boiling water, and though the surface tension is also reduced with increase of temperature, the adhesion is reduced much more quickly. The surface tension becomes zero at the critical temperature; the adhesion probably falls to a very low value at the boiling-point.

In order to get concentration by flotation, it is necessary to have an ore whose valuable constituent is some "greasy"

sulphide,* such as galena, or at most so automatically attached to the greasy sulphide that it comes off with it. Zinc sulphide is thus easily raised by galena when intimately associated, as in the Broken Hill and some of the Vieille Montagne Company's ores.

It is not enough to have the greasy particles; it is necessary to produce the gas-bells and get them against the particles. In practical work the only gas that comes off is carbon dioxide, and this appears to come largely from calcite. But mixing calcite with an ore which has a greasy constituent will not necessarily float it; the gas is apt to come away from the particles of calcite without getting attached to the ore. It seems much more likely that the gas that really effects the flotation is generated by the action of acid on small quantities of carbonates produced by a slight weathering of the ores. It is most likely due to small amounts of carbonate of iron and manganese. These carbonates are also not attacked by dilute acid in the cold.

But there is another consideration. The question of adhesion and of formation of adherent gas-bells is intimately connected with the air-film. Most, if not all, substances condense a volume of air or water, or both, on their surfaces. An extreme case of this is the absorption of hydrogen gas by palladium. No compound is formed here, because, according to Roozeboom, the amount of gas absorbed at any particular temperature is *not* constant, but varies with the pressure. Other elements, e.g., vanadium, nickel, and copper, also absorb small quantities of hydrogen, but in no case does the amount of gas absorbed bear any simple atomic ratio to the amount of metal. Thus vanadium absorbs 1.3 per cent of its volume of hydrogen, electrolytic zinc a few hundredths of 1 per cent, copper wire 0.306 vol., ordinary porous nickel absorbs 165 vols. of hydrogen, but loses it again in two to three days, and so on. These solid solutions, occlusions, or condensations, whatever they may be, must be carefully distinguished from the true hydrides, such as those of the alkali metals. The condensation of gases on solid surfaces and the great persistence of the film is especially familiar to workers with high vacua. A glass bulb, for instance, on exhaustion keeps on giving off gas for days. If the bulb is heated as strongly as the glass will bear, the gas comes off much more quickly. A Ruhmkorff discharge also brings it off. If the bulb, while still exhausted, is washed or filled with mercury, it will sweep the gas off the glass ("Incandescent Lamp Manufacture," *Electrician*, 1887). The electrodes also give off gas on sparking the tubes, and this gas cannot be got rid of by exhausting the tubes. Very many observers have noticed and described this nuisance. Aluminium is especially obstinate as shown by the experiments of Callendar. The literature is to be found in Kayser's "Handbuch des Spektroskopie," vol. i., pp. 239-243. This air-film seems to be intimately connected with the small adhesion for water. It may be that the air-film is itself the result of adhesion for gas, which is able to condense the gas on the surface. It cannot be any simple action of that sort, however, for time has great influence. Thus the gas comes off the inside of the exhausted globe very slowly, as already mentioned. On the other hand, small metal objects will float on water. Interesting experiments in this direction are recorded by Mayer (*Science*, 1896, [2], iv., p. 298). He floated rings of various metals—aluminium, iron, tin, brass, copper, lead, and German silver—made of 1 m.m. diameter wire and 50 m.m. in diameter, on water. The metals, however, must be clean and dry. If, after one of these rings has been sunk in water, it be dried and the experiment repeated, it will be found impossible to float the ring. After leaving it in the air for half-an-hour or so, it can be

* This effect of greasiness was well shown by the following experiment. Some ordinary steel filings, which probably had some oil on their surface, were immersed in dilute acid. Hydrogen was evolved round the particles, which were kept dry by the oil, large bubbles rose to the surface and burst, leaving absolutely dry filings on the top of the liquid. Clean new filings did not show this phenomenon.

again floated. Similarly a heated platinum ring will not float immediately after cooling, but will do so after lying in the air for a short time. This shows that the film takes time to form. Another way of demonstrating the presence of the gaseous envelope is to shift some powdered substance which easily sinks, such as sand or ferrous sulphide, on to the surface of hot water, previously freed from gas by boiling. Bubbles of gas rise from the surface of the solid particles.

Many observers have recorded the floating of perfectly dry sand on water. Among these may be mentioned Simonds (*Amer. Geol.*, 1896, xvii., 29; and *Science*, 1900, [2], xi., 510), Ladd (*Amer. Geol.*, Nov., 1898), Graham (*Am. Journ. Sci.*, 1890, [3], xl., 470), Nordenskiöld (*Nature*, 1900, lxi., 278), Carus-Wilson and Evans (ii., p. 318), and perhaps others. Evans also found that pieces of slate $1.5 \times 0.75 \times 0.1$ c.m. float on tap-water, if perfectly dry.

According to Simonds, the floating of the sand depends on the shape of the grains. Ladd notes the same condition, and adds that the pieces must be sharply angular. Felspar and mica will also float under these conditions.

Spring (*Bull. Soc. Belg. de Geol.*, 1903, xvii., 13) has made some experiments on the wetting of sand, and finds that it depends chiefly on the capillary-constant of the liquid and on the fineness of the particles.

However, the substances usually known as gangue are much more easily wetted than the metallic substances. Again, some are much more easily wetted than others. Thus, iron pyrites is easy to wet; that is to say, difficult to float, whereas antimony sulphide is difficult to wet, or easy to float.

A particle which is once wetted will never float, because even if a gas bubble were formed on or round it, it would not carry the solid up, as it falls through. On the other hand, if a particle has still a very thin film on it, but this is insufficient to buoy it up, it is easily conceivable that by generating gas, such as CO_2 , upon it, this gas will add itself to this small air-film and eventually raise the particle. Here, again, the temperature seems to be of importance, and this probably explains why a substance like ferrous carbonate, which is not attacked by dilute acid at a low temperature, is better than calcite or copper carbonate which are attacked in the cold.

Nothing is known about the thickness of the air-film or whether it is the same for all substances; or, as is more likely, variable. But it is very probable that for a given substance the thickness of the film is the same whatever the size of the particle; hence, only small particles can be raised without the addition of some other gas, such as CO_2 .

That the air does play an important part is shown in the case of stibnite and molybdenite. They can be concentrated by placing the ore in water nearly boiling. Apparently there is enough air on the surface of the particles to form with the steam a bell consisting of air and steam, which floats the particle. The air-film, or a surface with small adhesion, also gives a bell of gas or of steam a chance of forming. The surface tension makes it impossible for a bell of steam to start, as the bell is under extra pressure due to the surface tension, the pressure of the contained gas varying inversely as the diameter of the bell. Thus a bell of air, at ordinary temperatures, of 0.01 m.m. diameter has an extra pressure on it of 30,000 dynes per square centimetre, equal to a bead of about 30 centimetres of water. The explanation we offer—and it seems sufficient for the Potter process—is, therefore, that all solids have on their surface when dry a thin film of gas, probably air. Some of them—such as sand, quartz, carbonates—easily give up this film in water and become wet; whilst others, such as most metallic bodies, and especially the sulphides of lead, molybdenum, and antimony, have a smaller tendency to part with the film, and are not easily wetted. These can, therefore, be floated. If the air-film is insufficient to raise the particle, the flotation can be increased by the slow generation of gas on the particle. But if the particle has

once lost its air-film, that is to say, got wet, it can never be raised, and no amount of gas generated on it can help matters.

To sum up, we would suggest that the selective flotation is due to the presence of "greasy" sulphides, which have small adhesion, and that a high temperature is necessary to reduce the adhesion enough for the bells of gas to stick. It seems necessary that the gas should be produced at the surface of the particles themselves; and it is, in fact, produced by the decomposition of carbonates due to slight weathering of the ore. If an ore that can be floated is treated with acetic acid to remove the traces of carbonate, it cannot then be floated again. The air-film also plays an important part; and if an ore is thoroughly washed or boiled in water to remove the air-film, it cannot be concentrated with acid. Some ores, such as stibnite and molybdenite, appear to have enough air on their surface to form a mixture of air and steam at a temperature below boiling point, which has enough volume to float the particles. Acid is therefore unnecessary in such cases. Of the various ores and sulphides we have tried in dilute acid or acid sulphates of soda, the following are most easily floated in order of merit:—

Molybdenite.

Stibnite.

Galena.

Mixed zinc-lead sulphides, such as the Broken Hill ores.

Copper glance.

Zinc blende.

Iron pyrites.

The last two scarcely float at all. Copper glance only floats if slightly weathered, and then only in very small amounts.

With the Broken Hill ores the ratio of the Zn : Pb in the concentrate differs very little from that in the ore, only the gangue being left behind. Galena is fairly easy to float if finely ground, but owing to its rather high specific gravity very fine pulverisation is necessary to float it successfully. Stibnite and molybdenite go quite easily owing to their very greasy nature.

We have made a good many experiments with various ores, but do not think it is necessary to go fully into them here. We have therefore only given this short list as an example of the way in which things go.

We also tried some of the gangue obtained from the Broken Hill ores by the Phoenix process due to one of us. This looks like river-sand, and consists principally of rhodonites and garnets. Not the slightest flotation was obtained.

It is interesting to note that ground malachite—copper carbonate—floats fairly well in water. It may be remembered that this mineral has a peculiar greasy feeling. Beyond this, we have not found any other carbonates that float.

This list is only roughly correct, however, and it is most probable, in fact almost certain, that various samples of sulphides differ considerably; and if a slight weathering is necessary to produce the small trace of carbonate needed to give flotation, the "greasiness" in itself is not sufficient to give the separation. It is, in fact, quite impossible to tell beforehand which ores can be separated by flotation.

We have not gone much into the question of merits of the various solutions used for concentration by flotation. Potter originally used dilute acid, preferably sulphuric, of about 2 per cent strength. A saturated salt-cake solution is employed by another inventor, Delprat.

We have found that generally the latter solution works rather better than the former, and it has been suggested that this is due to the isohydric influence of the sodium sulphate on the sulphuric acid, thus driving back the dissociation of the latter, so that a saturated solution of salt-cake acts as a weaker acid than the dilute sulphuric acid itself. This is, however, not the case for several reasons:—1. The saturated salt-cake solution conducts considerably

better than the dilute acid. 2. It acts more violently on carbonates and iron than dilute acid. The degree of dissociation is, no doubt, considerably driven back, but as the total concentration in one case is so much greater than in the other, the actual concentration of the hydrogen-ions need not be less. In fact, it is only necessary to assume that the salt-cake solution is dissociated to about 5 per cent to make the H-concentration the same as that in 2 per cent acid where the dissociation is probably complete, or, at any rate, nearly so. All this is assuming there are such things as ions. With salt-cake solution the bubbles get larger than with dilute acid and rise more slowly owing to the greater density and viscosity of the former solution. Certainly a much more stable and compact scum is formed when salt-cake solution is used, and this is no doubt due to the viscosity of this solution, but more especially to the surface viscosity, which is always greater than the ordinary viscosity or internal friction. It is well known that bodies on the surface of a liquid attract one another if all be wet or all be dry. The former case does not concern us, as it only applies when the solid is lighter than the liquid. If one particle be wet and another dry then there is repulsion between them. The compactness of the scum in the case of salt-cake solution is therefore most likely due to the fact that the particles, on account of the increased surface viscosity as compared with dilute acid, tend to keep drier than with the dilute acid, and therefore attract one another, forming a compact scum. It need hardly be pointed out that this apparent attraction is really a surface tension phenomenon again. If particles of dry sand rest on water, each produces a little dent in the surface, and increases its area. The increase of area of the tense surface is least when the particles are altogether, making one big dent. This holds good—to a less extent—with greasy particles floating and with completely wet particles. With wet particles the dents become prominences, but the surface action is otherwise the same.

As regards the actual values of the surface tensions of water, dilute acid, and saturated salt-cake solution, there is very little difference. Dilute 2 per cent sulphuric acid has the surface tension very little smaller than that of water, and the same can be said of the salt-cake solution. The temperature coefficient for water and dilute acid is about the same. It is given by the formula $T_t = T_0 - 0.002t$. For salt-cake solution, the coefficient is practically zero. We have tried no other solutions, and are therefore not in a position to give any general explanation for the behaviour of various solutions. All we have tried to do is to sketch a rough explanation dealing broadly with the physics of ore flotation.

We are indebted for many facts to Mr. Blount and Prof. Huntington, who have both given much attention to the flotation of ores.

Study of an Industrial Cuprosilicide.—Paul Lebeau. —M. Vigouroux, in 1896, prepared a compound of copper and silicon by heating a mixture of the two elements containing 10 per cent of silicon, the composition corresponding to SiCu_2 . In 1901, he obtained an ingot containing less than 5 per cent. The author in his researches on metallic silicides used an industrial silicide of copper containing 50 per cent of silicon, and after describing the appearance and chemical properties he comes to the conclusion that the limit of combination of copper with silicon is not represented by SiCu_2 , but approaches to the formula SiCu_4 containing 10 per cent of combined silicon. He is curious to know how the silicification of copper varies with different conditions and proposes to continue his investigations. *Comptes Rendus*, cxli., No. 22.

Erection of Steel Chimneys.—Thomas Piggott and Co., makers of pipes, tanks, and steel structures, have just successfully completed two steel chimneys in South Wales, one 175 feet high and the other 125 feet high.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 7th, 1905.

Prof. R. MELDOLA, F.R.S., President, in the Chair.

(Concluded from p. 293).

209. *The Action of Ultra-violet Light on Moist and Dried Mixtures of Carbon Monoxide and Oxygen.* By SAMUEL CHADWICK, JOHN EDWIN RAMSBOTTOM, and DAVID LEONARD CHAPMAN.

The chemical effects produced by the passage of the electric discharge through gases are the result of at least three distinct causes, namely, (1) the cathode rays, (2) ultra-violet light, (3) catalytic action of the electrode and in particular the cathode. Ultra-violet light alone has been shown by Leonard to act on oxygen with the formation of ozone. The authors working with a quartz mercury lamp, with which 3 per cent of ozone could be produced from pure oxygen, have obtained the following results. A mixture of equal volumes of carbon monoxide and oxygen dried with sulphuric acid and submitted to the action of ultra-violet light, contracted at first slowly, and then more rapidly, until a maximum rate of decrease of volume was attained. The rate of contraction then gradually decreased, and finally became so slow that the experiment was stopped, and the composition of the gases found by analysis. It was ascertained that 22.95 per cent of the carbon monoxide had been converted into carbon dioxide, and that 39.63 per cent of the original oxygen had been changed into ozone.

A mixture of equal volumes of carbon monoxide and oxygen dried with phosphoric oxide behaved in almost the same way as the mixture which had been dried with sulphuric acid alone. When the contraction had reached approximately the same value as in the last experiment, it was found on analysis that 19.42 per cent of the total carbon monoxide had been converted into carbon dioxide, 37.48 per cent of the original oxygen being this time changed into ozone.

With the same mixture saturated with water vapour at 16°, the result was markedly different. The rate of contraction was practically uniform throughout the experiment, and this rate was less than half the value of the maximum rate with the dried mixture. When the total contraction had reached almost the same value as in the two previous experiments, it was found that 53.2 per cent of the carbon monoxide had been converted into carbon dioxide, and only 2.6 per cent of the oxygen into ozone.

If the first action of the ultra-violet light is conceived as consisting of a breaking up of the oxygen molecules into atoms, the atoms of oxygen thus formed prefer to combine with the molecules of carbon monoxide when the gases are moist, but with oxygen molecules when the gases are dry. In the present case, the rate of chemical change, measured by the contraction, is not accelerated by the presence of moisture, but the course of the reaction is determined by the hygroscopic condition of the mixture.

210. *Benzoyl Derivatives of Salicylamide.* By ARTHUR WALSH TITHERLEY.

Doubt has been thrown by Einhorn and Auwers on the formula $\text{BzO} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{NH}$, attributed by Titherley and Hicks, (*Trans.*, 1905, lxxviii., 1207) to the stable benzoylsalicylamide (m.p. 208°) originally obtained by Gerhardt and Chiozza (*Ann. Chem. Phys.*, 1856, xlv., 139), and which is produced by rearrangement even at 15 from the labile *O*-benzoylsalicylamide, $\text{BzO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH}_2$ (m.p. 144°), recently isolated by Titherley and Hicks.

Einhorn, in conjunction with Schupp (*Ber.*, 1905, xxxviii., 2792), and also with Haas (*Ber.*, 1905, xxxviii., 3628), considers the stable substance to be the *N*-benzoyl derivative, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NHBz}$, as also does Auwers (*Ber.*, 1905, xxxviii., 3256), who regards the rearrangement as due

to the wandering of the benzoyl group from O to N: $\text{BzO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$ (labile, m. p. 144°) $\rightarrow$ $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NHBz}$ (stable, m. p. 208°). The change would be analogous to that which takes place when attempts are made to isolate *O*-acyl-*o*-hydroxy-aromatic amines of the type $\text{AcO}\cdot\text{C}_6\text{H}_4\cdot\text{NHR}$ and $\text{AcO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NHR}$, where rearrangement occurs leading to the production of the *N*-acyl derivatives.

If the *N*-benzoyl formula be ascribed to the substance (m. p. 208°), it must be looked on as possessing anomalous properties; thus, it gives no ferric chloride reaction, is not decomposed by ammonia, like $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NHBz}$, and in other ways does not behave like an *N*-benzoyl derivative. Further, on heating with phosphorus oxychloride, it yields benzoylsalicylnitrile, which favours the *O*-benzoyl formula, thus:



Further investigations are proceeding with a view to elucidating the correct constitution of the substance.

211. "The Constitution and Colour of Diazo- and Azo-Compounds." By ARTHUR HANTZSCH.

In the August number of the *Transactions*, Armstrong and Robertson published a paper under the title: "The Significance of Optical Properties as Connoting Structure" (pp. 1272—1297), in which my theory of the stereochemistry of the diazo-compounds is criticised, and the remarkable conclusion expressed, that the "Hantzsch-Werner hypothesis" (in reality, so far as concerns the diazo-compounds, the "Hantzsch hypothesis"), "besides being an intangible and improbable conception, is unnecessary in fact."

If such an expression of opinion were correct, it would certainly not be without some significance, whilst the same holds conversely if such a view is shown to be incorrect, or at all events founded on a false basis. Since the latter is the case, it will be readily admitted that such a refutation ought also to find a place in the Society's publications.

The facts on which I venture to base this statement are simply the various researches on the subject, which I have published in the pages of the *Berichte der deutschen chemischen Gesellschaft*, a synopsis of which is to be found in a small published brochure, "*Diazoverbindungen*," F. Enke, Stuttgart, 1902.

The delay in replying is due to the fact that I only became acquainted with Armstrong and Robertson's work at the beginning of November.

Armstrong and Robertson proceed from the assertion that "all compounds containing the group $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{X}$ must be coloured" to the conclusion (p. 1280) that "all compounds of the type $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{X}$ should be coloured, and consequently only coloured diazo-compounds can be represented by such a formula. The formula assigned by Hantzsch to the so-called normal and isodiazotates are at once ruled out of consideration by this argument, as both these classes of compounds are colourless;" in other words, the latter do not correspond to the structural formula $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{OK}$.

It must first be observed that all chemists from Kekulé onwards, who have worked on diazo-compounds, must therefore have employed an incorrect formula, for they all, before as well as after the discovery of diazo-isomerism, accepted the formula $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{OK}$ for at least one of the two isomerides. But apart from this, Armstrong and Robertson's assertion can readily be shown to stand in contradiction to the facts, for according to their views the nature of an azo-compound as such is established by the fact that the compound is a coloured substance, and, conversely, a particular substance cannot be an azo-derivative because it is colourless. Such a conclusion has up to the present proved totally unacceptable, for Thiele's well-known extensive researches (*Annalen*, 1896, ccxc., 1) have shown that both coloured and colourless azo-compounds exist in the aliphatic series; for instance, the deep red azo-dicarboxylic ester, $\text{CO}_2\text{R}\cdot\text{N}:\text{N}\cdot\text{CO}_2\text{R}$, and the colourless azo-

iso-butyric acid derivatives, $\text{CRME}_2\cdot\text{N}:\text{N}\cdot\text{CRME}_2$. When Armstrong and Robinson proceed "being colourless, the diazo-salts cannot be formulated as diazene ($-\text{N}:\text{N}-$) compounds" (p. 1280), it is certainly logical to assert "that being colourless these so-called azo-compounds of the aliphatic series cannot be compounds of the type $-\text{C}:\text{N}:\text{N}\cdot\text{C}-$."

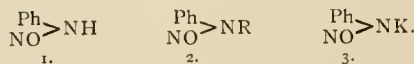
So long, therefore, as Armstrong and Robertson do not offer any explanation of these facts, or substitute other constitutional formulæ for these colourless compounds, regarded generally as azo-derivatives, just so long will their conclusion, namely, "that diazotates being colourless cannot have the ordinary formula $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{OK}$," remain unacceptable. But amongst the diazobenzene derivatives there also exist true chemical compounds containing the group $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{X}$; these, therefore, according to Armstrong and Robertson, must be coloured, but in reality they are colourless. For example, amongst the nitro-*isodiazobenzene* esters we have the nitro-diazo-ester, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{O}\cdot\text{CH}_3$ (von Pechmann, *Ber.*, 1894, xxvii., 672), which, to quote the author's description, "in the pure state is perfectly colourless." Here again it is necessary for them to replace the formula by a more suitable one, or their conclusions must necessarily be regarded as incorrect.

According to their view, "the normal diazotates must perforce be regarded as *diazonium derivatives*;" I do not consider it necessary to disprove this statement, and will content myself by pointing out that even Bamberger has given up the diazonium formula for the labile diazotates (*Annalen*, 1900, cccxiii., 98), and that his last attempt to rehabilitate it (*Ber.*, 1903, xxxvi., 4054) has been shown to be unwarranted (*Ber.*, 1904, xxxvii., 1084).

As regards the proposed formulæ for the *isodiazotates* (p. 1282), $\text{Ph}\cdot\text{N}-\text{N}\cdot\text{K}$ or $\text{Ph}\cdot\text{NK}\cdot\text{NO}$, the same remarks

apply. I discussed these formulæ at length some considerable time ago, and showed them to be unsatisfactory, and they have, as a matter of fact, been abandoned by all chemists who have studied experimentally the chemical behaviour of these substances. The two formulæ of Armstrong and Robertson also stand in contradiction to the fact that the previously-mentioned diazo-ester, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{OCH}_3$, can be obtained from the *isodiazotate*, so that in consequence the existence of a third hydroxyl form must be accepted. These hydroxyl compounds ($\text{Ph}\cdot\text{N}:\text{N}\cdot\text{OH}$) are not imaginary tautomeric substances, but real, definite, chemical compounds, for in conjunction with W. Pohl (*Ber.*, 1902, xxxv., 2964) I have shown that from the colourless *isodiazotates* there is formed, primarily, the free *iso*-(anti)diazohydroxide as a colourless, true acid, the general behaviour of which certainly indicates the presence of an (OH) group.

Armstrong and Robertson must therefore suggest another "hydroxyl formula" in place of $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{OH}$, and the fact cannot be too plainly pointed out that in accepting the nitrosoamine formula for the *isodiazotates* they again immediately stand in contradiction to their fundamental doctrine on the relation of colour to constitution, for, as is well known, most of the true secondary nitrosoamines, and nitrosoamine derivatives, are coloured. The indifferent primary nitrosoamines obtained as *pseudo*-acids by W. Pohl and myself through intramolecular charge of the diazohydroxides are also coloured, although as a logical consequence from Armstrong and Robertson's nitrosoamine formula (that is, absence of the group $\text{Ph}\cdot\text{N}:\text{N}$) these *isodiazotates* should be colourless if they were really nitrosoamine salts. As is seen from the three formulæ:—



by simple substitution of K for H or R, we obtain from the coloured substances (1) and (2) a colourless potassium salt (3), a result which is again incompatible with Armstrong and Robertson's theory.

(The reference to Dobbie and Tinkler's work (*Trans.*, 1905, lxxxv., 277); and *Proc.*, 1905, xxi., 75), namely, "that the salt $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{OK}$, in respect to its absorption spectrum, behaves as a nitrosoamine, and not as a diazo-salt," stands in marked contradiction to all its chemical properties. This being so, too much weight cannot be attached to this evidence until it has been ascertained, for example, how the isomeric esters $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{O}\cdot\text{CH}_3$ and $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{CH}_3)\cdot\text{NO}$ behave under similar conditions, a point which the above-named chemists, at my request, have most kindly promised to investigate).

The whole of Armstrong and Robertson's views on the normal diazosulphonates and diazocyanides are quite incorrect. They state (p. 1281) "the action of sulphite may be supposed to involve in the first place the formation of a diazonium sulphonate, $\text{R}\cdot\text{N}^+\cdot\text{SO}_3\text{K}$," and, so far as

I can understand, also put forward the formula $\text{Ph}\cdot\text{NH}\cdot\text{SO}_3\text{K}\cdot\text{NOH}$. The latter formula is impossible, because most diazosulphonates correspond to the formula $\text{Ph}\cdot\text{N}_2\cdot\text{SO}_3\text{K}$; that is, to one containing no water. The diazonium formula itself stands in contradiction to their theory, for if the appearance of colour denotes a change in constitution, and if all the sulphonates of colourless metals (namely, those of silver and mercury) are colourless, why is it that the diazonium sulphonates formed from the colourless diazonium and sulphonic acid components possess an intense orange colour? From the very fact that the labile equally with the stable sulphonates are coloured, they must both be azo-compounds, $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{SO}_3\text{K}$.

The statement that "the so-called *syn*-compound sulphonates and cyanides may well be simple equilibrated mixtures of diazonium cyanides and sulphonates with the stable *anti*-compounds" (p. 1283) is controverted by the facts, for all the normal diazocyanides exhibit analogous behaviour with water and cuprous oxide, but in a manner quite different from that of the *isodiazo*cyanides. Further, as regards their colour and constitution, the labile *syn*-diazocyanides and diazo-sulphonates are always more intensely coloured than the stable *anti*-forms. All diazonium sulphonates are colourless, and all diazosulphonates should be colourless; so that Armstrong and Robertson's view leads to the remarkable result that, by the addition of a colourless to a coloured substance, the colour intensity of the resulting mixture is increased—certainly the greatest *contradictio in adjecto*. In addition, Armstrong and Robertson have not sufficiently taken into consideration the fact that the labile cyanides are distinct chemical compounds possessing definite unchangeable properties, that is they are not chemical mixtures. The explanation of the change of the *syn*- into the *anti*-form (p. 1281) is impossible by reason of the assumption that an addition of the elements of water takes place, with a subsequent splitting off of the same elements, for in reality many *syn*-sulphonates and very many *syn*-cyanides isomerise in the solid state or in anhydrous solvents.

In short, therefore, the whole of Armstrong and Robertson's conceptions with respect to labile diazo-isomerism are impossible, and their remark that my "*syn-anti*-conception is based upon a false use of the principle of analogy" will certainly be considered as more applicable to their own untenable theories, according to which "the stereochemistry of the diazo-compounds is unnecessary in fact."

With such statements as "in the case of the diazosulphonates, it is clear that they differ essentially in type," put forward without the support of a single experimental fact, equally without any theoretical explanation, discussion is out of the question, and, in fact, would be superfluous.

It is unfortunately necessary for me to make an emphatic protest in reference to Armstrong and Robertson's remarks (p. 1280) on the small value which ought to be placed on the analytical results of the labile diazo-isomerides. One

has the right to expect that before such statements are made reflecting on the accuracy of the work in question, the greatest care has been taken to verify the facts. That such a sweeping assertion is altogether unwarranted will, I think, be admitted from a consideration of the following points:—

1. *Labile Diazotates*.—The labile diazotates certainly always contain small quantities of alkali (*Ber.*, 1901, xxxiv., 2159; 1902, xxxv., 2969) or water of crystallisation (*Ber.*, 1895, xxviii., 2006; 1896, xxix., 1077), but in the form of their crystalline salts they have been obtained quite pure, so that no chemist who has worked on the subject, from Kekulé onwards to Bamberger, has ever seriously questioned the accuracy of the empirical formula ArN_2OK for the diazotates.

2. *Labile Diazosulphonates*.—The numerous concordant analyses on these substances (*Ber.*, 1894, xxvii., 3529; 1897, xxx., 76, 80—81) prove undoubtedly the accuracy of the formula $\text{PhN}_2\text{SO}_3\text{K}$ for this substance. It is true there is generally present a small quantity of the *anti*-salt, formed by spontaneous isomerism of the *syn*-derivative, but this certainly does not come into question as affecting the accuracy of the formula or as regards the facts of the isomerism.

3. *Labile Diazocyanides*.—The fact must be emphasised that many of these compounds can without difficulty be very readily obtained and isolated in a pure state (*Ber.*, 1896, xxix., 666; 1897, xxx., 2530), so that their constitution as chemically individual substances cannot be doubted. They are not to be regarded therefore as "eminently unstable" and "impure," as Armstrong and Robertson assert. As a matter of fact, some of the *syn*-derivatives are so stable as to be only convertible with difficulty into the more stable isomeric *anti*-form.

The undoubted existence of these two classes of compounds (the representatives of the stereo-isomeric azo-compounds), which Armstrong and Robertson do not admit, provides therefore the strongest proof for my stereochemical theory of the diazo-derivatives, a theory supported by a large mass of experimental evidence, in connection with which the theoretical signification has always been carefully pointed out. The reflection by Armstrong and Robertson on the accuracy of this work is altogether unwarranted, and with a thorough knowledge of the subject, it is impossible for me to understand how such assertions could be made.

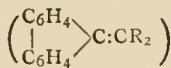
I am forced to conclude that they have not thoroughly informed themselves in respect to my experimental investigations. Above all, I have to deplore that the numerous exact analytical results already published should thus be brought into discredit, and the stereo-chemistry of the diazo-derivatives founded on them regarded as "unnecessary in fact"; to be replaced by a view with which the facts, indeed the principle itself, stand in direct contradiction.

In reply to the statement that "I am opposed in principle to conclusions based on optical evidence" (*Ber.*, 1899, xxxii., 3149), it is only necessary for me to say that such conclusions in regard to constitution are not warranted from a mere consideration of the optical properties, more especially when these stand in contradiction to the general chemical behaviour of the substance.

It is certainly a very great surprise to me that such a statement should be brought forward, for I have always regarded the physico-chemical behaviour of the substance as of very great importance, and especially in relation to the colour of substances as denoting their constitution. Thus, some eighteen years ago, in conjunction with Hermann (*Ber.*, 1887, xx., 2801), I was one of the first to draw attention to the relation between colour and constitution in the case of desmotropic substances, and recently, as a result of my researches on pseudo-acids, I have been able to show experimentally that the appearance of colour in the formation of coloured alkali salts from hydrogen compounds is due to an intramolecular change taking place in the position of a hydrogen atom. I intend publishing

shortly an account of several researches dealing with the relation of colour to constitution, and in particular establishing the quinonoid structure for nitrophenols, a theory first put forward by Armstrong on very slender experimental evidence, and certainly not accepted by a large number of chemists at the present time.

Summarising, it is my firm conviction that the colour of substances is one of the most important criteria in the characterisation of their constitution, but at the same time it is also one of the most delicate and subtle. Unfortunately, it is in so very many cases quite impossible to explain the origin of the colour, or to account for the remarkable phenomena by structural formulæ. It is only necessary to recall the existence of the coloured fulvene, of the coloured diphenylene-ethylene derivatives—



on the one hand, and the colourless polyacetylene on the other; of the coloured derivatives of diethoxynaphthostilbene, dibenzoylethylene, and benzaldehydobenzoin compared with their colourless isomeric modifications.

In short, as pertaining in particular to the azo- and diazo-derivatives considered in the light of their chemical and physical properties, there exist both *coloured* and *colourless* azo- and diazo-compounds, the cause of which colour is unknown, and which, although representable by Baeyer's valency formulæ ($\text{Ph}\cdot\text{N}:\text{N}:\text{R}$ colourless, $\text{Ph}\cdot\text{N} \approx \text{N}:\text{R}$ coloured), remain still unexplained by any rational structural formulæ. Above all it should not be overlooked that a sharp line of demarcation between coloured and colourless substances does not exist either theoretically or practically; for the same complex appears in an intensely coloured, a pale coloured, or a colourless substance, according to the nature of the groups associated with it. Thus, in the case of the aromatic azo-complex $\text{Ph}\cdot\text{N}:\text{N}$, when this is attached to nitrogen the colour-intensity of the products is less than when it is attached to carbon (thus, $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ possesses a lighter yellow colour than $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{CN}$ or $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{Ph}$). It is therefore comprehensible that when the same complex is attached to oxygen (as in the diazotates $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{OR}$) we have a colourless substance formed, more especially as the diazo-compounds containing the group $\text{RO}\cdot\text{N}:\text{N}\cdot\text{OR}$ (for example, hyponitrous acid, salts, and esters) are also colourless.

We have accordingly in the following series of colour intensities:—

$\text{Ph}\cdot\text{N}:\text{N}\cdot\text{OR}$	$\text{Ph}\cdot\text{N}:\text{N}\cdot\text{NHR}$	$\text{Ph}\cdot\text{N}:\text{N}\cdot\text{CN}$
Colourless.	Pale coloured.	Intensely coloured.

a collection of facts which we cannot explain or represent satisfactorily by structural formulæ.

The change of condition from the coloured to the colourless state in azo-compounds is bound up with, but not, however, altogether dependent on, the known structural and stereochemical isomerism of the diazo-derivative; that is, presence or absence of colour is not definitely decided by such isomerism; for whilst both classes of the stereo-isomeric diazotates are colourless, both those of the stereo-isomeric diazosulphonates and diazocyanides are coloured. Since Armstrong and Robertson's views and formulæ are quite untenable, the older structural and stereochemical formulæ indicate now, as before, the best and most accurate representation of the facts concerning the diazo-compounds.

212. "Note on the Incandescent Mantle as a Catalyst and its Application to Gas Analysis." By JOHN ERNEST MASON and JOHN WILSON.

The method described by Lewes (CHEMICAL NEWS, 1905, xci., 61) for demonstrating the incandescence of the ordinary gas mantle in a cold mixture of coal-gas and air may also be employed with a mixture of ammonia vapour and air. The authors described a modification for showing the incandescence of the mantle in an unburnt mixture of

alcohol vapour and air. Although less effective, the mantle may be used as a substitute for platinised asbestos in the ordinary lecture experiments for preparing formaldehyde from methyl alcohol vapour and air, and sulphur trioxide from sulphur dioxide and oxygen.

Fragments of mantle in a hard glass or preferably quartz tube may be used in place of palladium or palladium-asbestos, for the estimation of hydrogen and carbon monoxide in gas analysis by combustion with excess of air or oxygen. Methane and mixtures of methane and hydrogen may be estimated similarly by passing these gases mixed with excess of oxygen over fragments of mantle heated in a quartz tube, and measuring the contraction after combustion and subsequent treatment with caustic potash solution. The results agree well with those obtained by the customary explosion methods. Good results may also be obtained by passing the gases mixed with oxygen over asbestos heated in a small quartz tube. Hydrogen, and less readily methane, may be estimated by passing the gas mixed with oxygen through narrow tubes of heated Jena glass alone.

213. "The Influence of certain Amphoteric Electrolytes on Amyolytic Action." By JOHN SIMPSON FORD and JOHN MONTEATH GUTHRIE.

An investigation of the influence of asparagine, glycine, and α -alanine on amyolytic action has led to the following conclusions:—

1. Asparagine and the amino-acids mentioned have no specific influence in augmenting the action of amylase; the apparent augmentation of action sometimes obtained by the addition of these amphoteric substances (or of feeble acids) is due to their neutralising alkaline (or other) impurity in the starch or enzyme solution.

2. Normal amyolytic action takes place in neutral solution. In the plant substance, this neutrality is brought about by equilibrium between the basic and acid products present.

3. Until the conditions influencing the action of enzymes are more fully established, it is inadvisable to formulate mathematical laws as to the kinetics of enzymic hydrolyses.

4. Purified soluble starch has the properties of an extremely feeble acid; it is capable of yielding negative ions under the influence of strongly positive ones.

214. "The Estimation of Picric Acid Additive Compounds." By FRANK STURDY SINNATT.

The method of Knecht and Hibbert (*Ber.*, 1903, xxxvi., 1549) for the estimation of picric acid by means of titanous chloride has been found to be applicable to other picrates, and also to picric acid additive compounds.

Twenty-five c.c. of a solution of 0.200 gm. of naphthalene picrate in 250 c.c. of alcohol were titrated with titanous chloride, and gave 99.49 per cent of naphthalene picrate. Pyridine and strychnine picrates yielded 100.19 and 99.69 per cent respectively.

In many cases it is convenient to dissolve the picrate in hydrochloric acid. The method has been applied to the estimation of naphthalene in coal-gas; the naphthalene picrate is separated by the usual process (Colman and Smith, *Journ. Soc. Chem. Ind.*, 1900, xix., 128), washed, dissolved in a small volume of alcohol, and titrated with titanous chloride. If a standard solution of picric acid is used in the wash-bottles, the filtrate and washings may also be titrated. The results compare with those obtained by Colman and Smith's method. The estimation of naphthalene and the applications of the titanous chloride process to other picric acid additive compounds are being continued, and the results will be embodied in a further communication.

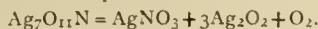
215. "Silver Dioxide and Silver Peroxynitrate." By EDWIN ROY WATSON.

A black crystalline product, obtained at the anode during the electrolysis of an aqueous silver nitrate solution, was considered by Ritter to be silver dioxide, Ag_2O_2 (*Gehlen's Neues Journ.*, 1804, iii., 561). Later investigations showed

that it could not be regarded as silver dioxide, and a variety of conflicting formulæ have been proposed.

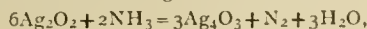
The author has electrolysed aqueous silver nitrate with different current strengths and densities, and with solutions of varying concentrations, and has analysed the product formed at the anode in order to see whether this should be regarded as a definite chemical compound or as a mixture, the composition of which varies with different conditions. It was concluded that the product was a definite chemical compound, and that its composition was correctly represented by Sûlc's empirical formula $\text{Ag}_7\text{O}_{11}\text{N}$. The substance is easily decomposed by heat or when left in contact with water or organic matter, such as filter-paper, and to this cause must be attributed the divergent results of the earlier investigators.

This compound, silver peroxynitrate, as it has been termed by Tanatar, on boiling with water decomposes in accordance with the equation—



Silver dioxide is a greyish black powder (sp. gr. 7.44), which may be heated to 100 without decomposition. At higher temperatures it gently decomposes into its elements. It dissolves in hot dilute sulphuric acid in accordance with the equation $2\text{Ag}_2\text{O}_2 + \text{H}_2\text{SO}_4 = 2\text{Ag}_2\text{SO}_4 + 2\text{H}_2\text{O} + \text{O}_2$.

Its behaviour with ammonia is noteworthy, and may be represented in the following manner:—



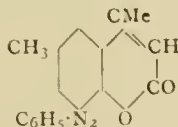
so that the compound in solution must be regarded as a polyvalent silver compound, probably $\text{mAg}_4\text{O}_3 \cdot \text{nNH}_3$.

The dioxide of silver and silver peroxynitrate both dissolve in cold concentrated nitric acid with the production of an intensely brown solution, the colour of which gradually fades even at the ordinary temperature, and much more rapidly on warming. The rate of decomposition of the compound is proportional to its concentration in the solution, a fact which makes it impossible to give to the compound the simple formula $\text{Ag}(\text{NO}_3)_2$. The formulæ $\text{Ag}_4(\text{NO}_3)_8$ and $\text{Ag}_2(\text{NO}_4)_2$ are, however, possible.

216. "The Constitution of *o*-Hydroxyazo-compounds. Preparation of Benzeneazodimethylcoumarin." By JOHN THEODORE HEWITT and HERBERT VICTOR MITCHELL.

The authors have hydrolysed the 4 : 6-dimethylcoumarin described by Pechmann and Cohen (*Ber.*, 1884, xvii., 2118), and have coupled the alkaline coumarinate so obtained with phenyldiazonium chloride and the three nitrophenyldiazonium salts.

The alkaline azocoumarinates so obtained are highly coloured, varying in shade from red to violet. On acidification, light coloured anhydrides of the type—



are precipitated.

This instantaneous dehydration indicates the existence of a ready-formed hydroxyl group, even in the *o*-hydroxyazo-series.

Benzeneazo-4 : 6-dimethylcoumarin melts at 199—200°; the *o*-, *m*-, and *p*-nitrobenzeneazo-4 : 6-dimethylcoumarins melt at 240—250° (with decomposition), 212° and 229° respectively, these melting-points being corrected.

217. "Caro's Permonosulphuric Acid." By THOMAS SLATER PRICE.

Hitherto it has not been possible to decide between the formulæ H_2SO_5 and $\text{H}_2\text{S}_2\text{O}_8$ for Caro's permonosulphuric acid. The decision could readily be made if a pure salt, for example, the potassium salt, could be obtained. The simplest method would be to heat a weighed quantity of the salt and determine the weight of potassium sulphate left; this weight would depend on whether the formula was KHSO_5 or $\text{K}_2\text{S}_2\text{O}_8$.

The author has not yet succeeded in preparing the pure potassium salt, but a mixture has been obtained containing the potassium salts of sulphuric, permonosulphuric, and perdisulphuric acids, and also potassium hydrogen sulphate. It was found possible to determine the amounts of each of the constituents present, and thus calculate the weight of potassium sulphate which would be left on heating up a known weight of the mixture; this could then be compared with the actual weight found. The results obtained point to the formula H_2SO_5 as the correct one.

NOTICES OF BOOKS.

Qualitative Chemical Analysis, Organic and Inorganic. By F. MOLLWO PERKIN, Ph.D. Second Edition. London, New York, and Bombay: Longmans, Green, and Co. 1905.

As some time has elapsed since the first edition of this book was published, it may be worth while to explain shortly its plan, which presents some novel features. The author has skilfully dovetailed in theory with practice, so that the student is obliged to think what he is doing, and is prevented from falling into a mechanical habit of work. The usual group tests are given, together with full analytical tables and schemes of separation; but the discussion of the results and the excellent summaries—as, for instance, in the case of the separation of arsenic, antimony, and tin—are characteristic features which mark the book out as specially valuable for training the student in good mental habits. Organic chemistry is treated at greater length than is usual in books of this kind, and copious additions have been made to this part in the second edition, which also contains considerably more theory than the original. The discussions of theory are interspersed among the practical work, and not, as a rule, placed apart—a plan which has many obvious advantages to recommend it.

Elementary Practical Metallurgy: Iron and Steel. By PERCY LONGMUIR. London, New York, and Bombay: Longmans, Green, and Co. 1905.

THIS work may be regarded as an elementary introduction to the study of the metallurgy of iron and steel which is intended specially for the beginner. The author has endeavoured to make the subject as attractive and interesting as possible, and lays most stress upon practical points of view, while the theory is neglected, except when it bears directly upon practice. The treatment is quite elementary, and seems to present no striking novelties in any direction, so much so that the reader is led to wonder whether the book will fulfil any special purpose not satisfactorily provided for in some of the numerous other books which have been written having practically the same scope and resembling it in many respects. The insistence upon practical methods and practical results is a good feature of the book, and the beginner, using it as an introduction which does not pretend to go into details, may safely trust to the author's accuracy.

Food Preservatives; their Advantages and Proper Use. By R. G. ECCLES, M.D., Phar.D. With an Introduction by E. W. DUCKWALL, M.S. New York: D. van Nostrand Co. 1905.

THE vexed question of the toxic effects of preservatives in food is discussed at considerable length in this book, and the sub-title, "The Practical *versus* the Theoretical Side of the Pure Food Problem," gives some idea of its scope and object. An account is included of the various preservatives in common use, but we notice some omissions in the list. For instance, no mention is made of the compounds of fluorine, although the use of ammonium fluoride in beer is by no means uncommon. Rough

methods of detection are given, but no estimation processes, nor are any notes on the sensitiveness of the various tests added. As regards the author's arguments in favour of the free use of preservatives, both partisans and opponents of the theories put forward must recognise the futility of heated writing in any form, especially in a scientific work of this kind, and also of the introduction of personal matters, which, after all, only concern the *bond fides* and accuracy of two authors, the writer of this book and the professor whose statement he calls in question. The impartial critic, after reading such a book, cannot fail to be convinced that those who hold diametrically opposite views must be possessed of very strong arguments to call forth such vehement criticism. It is typical of the author's mind and method that he compares those who disagree with him as regards the labelling as "adulterated" foods which contain preservatives, to the people who hunted down heretics in the olden times, and whose rancour was caused by the dislike of change in mental food, while the same quality of the modern heresy persecutors is caused by the dislike of the introduction of changes in man's physical food.

Modern Theory of Physical Phenomena. By AUGUSTO RIGHI. Authorised Translation by AUGUSTUS TROWBRIDGE. New York: The Macmillan Company. London: Macmillan and Co., Ltd. 1904.

THE Italian version of this work was much read, and it seems probable that the translation will be equally appreciated by a certain class of readers in England. Professor Righi's style is admirably suited for the production of such a work as this, for he has to a high degree the power of illustrating and explaining vividly and making the elementary treatment of a subject very readable and interesting. For the benefit of those whose scientific knowledge is slight he discusses the nature of electrons, cathode rays and ions, the phenomena of radio-activity, and the constitution of matter, explaining very clearly the chief features of the theory which has been built up on the basis of the observed facts. It requires no small skill to produce such an excellent elementary work, and Professor Righi is greatly to be congratulated on his interesting little book.

Introduction to the Study of Organic Chemistry. Second Edition. By JOHN WADE, D.Sc. (Lond.). London: Swan, Sonnenschein, and Co., Ltd. 1905.

THE plan of this book is thoroughly sound and the working out no less satisfactory. The author aims at inducing students to build the foundations of their knowledge of organic chemistry on facts which they have discovered experimentally, then deduce generalisations from these facts, and proceed to further experimental work suggested by these generalisations. Thus the student's knowledge should be thoroughly practical, and at the same time he would be training himself for research work and developing his logical faculties. Thus, as far as its aim is concerned, the book has very distinctive features, and we are not surprised to learn that the first edition was favourably received, for the details are admirably presented, and the treatment is decidedly original. Every care is taken to impress the essentials on the reader's mind, and the synoptical charts given at the end of nearly every chapter are admirably suited for this purpose. The number of these charts has been considerably increased in the new edition, and they are now provided for practically every series of important transformations and syntheses. Briefly, the plan is worked out as follows:—The first part deals with typical compounds of simple constitution, the nature and properties of some of the important classes of organic compounds being investigated, and the conception of the organic radical introduced and thoroughly explained. The second section deals with synthesis and molecular structure, which subjects are afterwards further developed in Section IV. Sections III. and V. to XVII. treat systematically

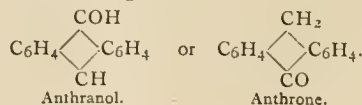
of the various classes of carbon compounds. Then follows one of the most useful parts of the book, that is the appendix of supplementary laboratory notes, which gives details of the preparation and purification of practically every compound which may advantageously be prepared by the student in the laboratory. This part has been much extended in the new edition, and now provides a complete course of practical organic chemistry, a short scheme of qualitative analysis having been added.

CHEMICAL NOTICES FROM FOREIGN SOURCES

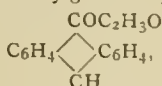
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxli., No. 22, November 27, 1905.

Distillation of Copper.—Henri Moissan.—The author has shown by previous researches that refractory bodies no longer exist, and that while certain compounds are decomposed by simple raising of temperature, others are formed at high temperatures—such as carbides, silicides, and borides—decomposing, according to M. Violle, at a temperature approaching 3500°. In his notes of 1892–1893, the author has shown that all metals can be volatilised in the electric furnace, and he has continued his researches in order to classify the boiling-points of certain metals, hoping that the physicists will be able to determine accurately these temperatures. In 1859 by Despretz, and in 1882 by Siemens and Huntingdon, it was shown that small quantities of copper volatilised by the heat of the electric arc at atmospheric pressure. In 1905 Kraft and Bergfeld showed that copper boiled at 1600° in the cathodic vacuum. The author, by using his electric furnace and following the experiments of Kraft and Bergfeld, heated 300 grms. of copper for five minutes in a current of 300 ampères under 110 volts. The metal melted, and after three minutes began to boil, the distillate being collected on a tube cooled by a rapid current of cold water. At the end of the experiment it was found that 50 grms. had been distilled. A second experiment gave 160 grms. in six minutes, and a third 233 grms. in eight minutes. The author describes in detail the appearance of the condensed product, finding it contains 99.76 per cent of copper, which behaves chemically exactly like copper filings. The deposit on a cylindrical receiver, placed over the perforated lid of the furnace, consisted of oxide of copper, quicklime, and black globules; consequently the copper vapour in contact with the air had burnt to little globules of black oxide, some of which enclosed a nucleus of red metal. The metal in the crucible contained small quantities of iron, lime, and aluminium, derived from the impurities in the electrodes, but far more important than this was the presence of graphite. This graphite—sometimes amorphous, sometimes crystalline—separated by nitric acid, washed, and dried, had a density of 2.12. By using a current of 800 ampères under 110 volts, and taking a crucible which can hold 8 to 10 k.grms. of copper, the author states that several kilogrms. may be distilled in a few minutes. He concludes:—(1) That copper is readily distilled by the electric furnace; (2) that when the vapour condenses on a cold surface, a filiform deposit of copper is obtained having all the properties of ordinary copper; (3) that at its boiling-point copper dissolves graphite, which separates out in more or less crystalline form on cooling.

Benzylidene Derivatives of Anthrone or Anthranol.—A. Haller and M. Padova.—Liebermann, in 1882 and 1887, isolated the compound $C_{14}H_{10}O$ from among the products of reduction of anthraquinone, and gave to it one or other of the following formulæ:—



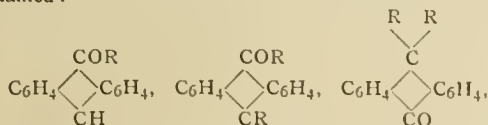
Since this compound readily gives acetyl-anthranol,—



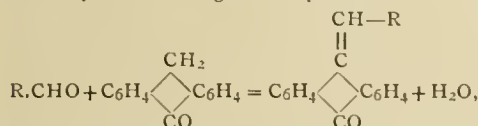
he decided in favour of the first formula. Later, Goldmann

showed that, with chlorine, the chloride, $\text{C}_6\text{H}_4 \text{---} \text{C}_6\text{H}_4$, $\begin{array}{c} \text{CCl}_2 \\ | \\ \text{CO} \end{array}$

is formed and (in another work) that, on treatment with potash and alcoholic iodides, the three following are obtained :—



the last evidently being a dialcylol derivative of anthrone, while the first two revert to anthranol. According to circumstances, then, the compound $\text{C}_{14}\text{H}_{10}\text{O}$ behaves either as a hydroxy-anthranol or a methylene derivative (anthrone), and in support of the latter is the formation of non-saturated compounds on condensation with aldehydes, according to the equation—



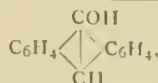
as in the case of benzylidene anthrone or dehydrobenzyl-oxanthranol, prepared at first by Levi, and later by C. Bach, by the dehydration of benzyloxanthranol obtained by acting on anthraquinone by benzyl bromide in the presence of potash and powdered zinc. The authors have succeeded in preparing this benzyloxanthranol from anthraquinone and the organo-magnesium compounds according to the method of Grignard, and also by using benzyl-magnesium chloride instead of the magnesium compounds of brominated benzene or toluene. With sulphuric acid it loses water and yields the benzylideneanthrone. *Condensation of Benzoic, Anisic, and m-Nitrobenzoic Aldehydes with Anthrone*.—This is effected with the help of piperidine, the solvent being anhydrous pyridine. 1. Benzylideneanthrone (dehydrobenzyl-oxanthranol) was prepared by the authors by heating for six hours a mixture of anthranol (prepared by the method of Liebermann and Gimbel), benzoic aldehyde, dry pyridine, and piperidine. Yellow needles were obtained, melting at $126-127^\circ$, soluble in alcohol, chloroform, and benzene, and insoluble in ligroin, and giving the composition of benzylideneanthrone; 36 per cent of the theoretical yield being obtained. 2. Anisylidene, or $p\text{-C}=\text{CHC}_6\text{H}_4\text{OCH}_3$

methoxybenzylideneanthrone, $\text{C}_6\text{H}_4 \text{---} \text{C}_6\text{H}_4$, $\begin{array}{c} \text{CO} \\ | \\ \text{C} \end{array}$,

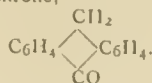
was prepared as the preceding. Crystallising from alcohol or acetic acid, yellow needles were obtained melting at $140.5-141.5^\circ$, and less soluble than the preceding in alcohol, acetic acid, acetic ether, chloroform, and benzene, and insoluble in ligroin. 3. *m*-Nitrobenzylideneanthrone, $\text{C}=\text{CHC}_6\text{H}_4\text{NO}_2$

$\text{C}_6\text{H}_4 \text{---} \text{C}_6\text{H}_4$, $\begin{array}{c} \text{CO} \\ | \\ \text{C} \end{array}$, was prepared under the same con-

ditions and crystallising from acetic acid, and then benzene; it melted between 165.5° and 166.5° . Chloroform, benzene, acetic acid, and warm pyridine dissolved it easily, but it was only slightly soluble in methyl and ethyl alcohols, and not at all in ligroin and petroleum ether. The authors conclude that $\text{C}_{14}\text{H}_{10}\text{O}$ is a tautomeric compound, for it behaves, under the above conditions, not as anthranol,—



but as its isomer, anthrone,—



The authors intend to extend their investigations towards other anthranols.

Berichte der Deutschen Chemischen Gesellschaft.

Vol. xxxviii., No. 15, 1905.

Electrical Preparation of Colloidal Solutions of Selenium and Sulphur.—Frich Muller and Romuald Nowakowski.—Already noticed.

Compounds of Chromium containing Pentavalent Chromium.—R. F. Weinland and Walter Fridrich.—If a solution of chromic acid is allowed to stand for some time in hydrochloric acid saturated at 0° some chlorine is evolved, and the liquid becomes dark reddish brown; when a solution of pyridine or quinoline in strong hydrochloric acid is added, after a short time brown-red glistening flakes are obtained. Analysis shows that they contain one atom of chromium to four atoms of chlorine and one molecule of pyridine (or quinoline), and by iodometric determination of the oxidation products of the chromium the authors found that two-thirds of the chromium in the compound is hexavalent and one-third trivalent. This corresponds to an oxide, $4\text{Cr}^{\text{VI}}\text{O}_3 + \text{Cr}_2^{\text{III}}\text{O}_3$ or $\text{Cr}_2^{\text{V}}\text{O}_5$, and the simplest assumption is that the compounds repre-

sent salts of a meta acid, $\text{Cr}^{\text{V}}\text{O}_3\text{H}$ or $\text{Cr}^{\text{V}}\text{O}_3\text{H}$, in which

two atoms of oxygen are replaced by four atoms of chlorine. This assumption was confirmed by the determination of the molecular weight of the pyridine salt cryoscopically in glacial acetic acid; this gives a molecular weight corresponding to the formula $\text{CrCl}_4(\text{OH})\text{C}_5\text{H}_5\text{N} \cdot \text{H}_2\text{O}$. As regards the stability of the compounds, the pyridine salt can be kept over sulphuric acid, but gradually decomposes in the air, turning yellow. The quinoline salt is much less stable, and rapidly becomes orange-red, and finally yellow in the air. If after the compound has become yellow, fuming sulphuric acid is added to it, it again becomes brown-red. Chlorine is evolved when the compounds stand in air, so that a part of the chromium must be reduced to the trivalent state. In strong hydrochloric and in glacial acetic acid the salts dissolve without decomposition. The aqueous solution is yellow, and gives with ammonia a precipitate of chromium hydroxide, and with lead acetate a precipitate of lead chromate. Thus we must assume that water splits the acid of pentavalent chromium into compounds of hexa- and trivalent chromium, the decomposition being exactly analogous to that produced by water in the case of manganic acid, when permanganic acid and manganese dioxide are formed.

Sodium Hydrosulphite.—A. Binz and W. Sondag.—Sodium hydrosulphite reacts with sodium thiosulphate, forming sodium sulphide. To ascertain the course of the reaction, the different forms in which the sulphur was present were determined quantitatively by the following experiments:—A weighed quantity of the powdered hydrosulphite was titrated with standard potassium ferricyanide in a current of carbon dioxide. This titration proved the presence of 80.2 per cent $\text{Na}_2\text{S}_2\text{O}_4$. Then from another weighed quantity the sulphur dioxide was removed by boiling with hydrochloric acid and carbon dioxide. The liquid was filtered from sulphur, and in the filtrate the sulphate sulphur was determined by precipitation as barium sulphate; this amounted to 0.93 per cent. A weighed quantity of the hydrosulphite was converted into tetrathionate, which, when boiled with hydrochloric acid and pure aluminium foil in a current of carbon dioxide, gave an

amount of sulphuretted hydrogen corresponding to 0.67 per cent thiosulphate sulphur. The sulphite sulphur amounted to 4.60 per cent, and was determined by shaking the substance with sodium hydroxide solution (1.7 per cent) in air, decomposing the thiosulphate with mercuric chloride, and driving off the sulphurous acid into $\frac{1}{10}$ N iodine solution. A portion of the hydrosulphite powder was then warmed to 57–62° for five hours in absence of air with sodium thiosulphate and caustic soda. The amounts of sulphur in the form of hydrosulphite, sulphide, sulphite, thiosulphate, and sulphate were then determined, and these were found to agree with the following equation, which represents the reaction between hydrosulphite and thiosulphate :—



Determination of Nitric and Nitrous Acids.—Jacob Meisenheimer and Friedrich Heim.—The authors have devised a method by which nitrous acid can be determined conveniently, quickly, and accurately, and which is well suited for the estimation of nitric and nitrous acids in presence of one another. The separation of the two acids rests upon the already known reactions represented by the following equations :—(1) $\text{HNO}_2 + \text{HI} = \text{NO} + \text{I} + \text{H}_2\text{O}$, (2) $\text{HNO}_3 + 3\text{FeCl}_2 + 3\text{HCl} = \text{NO} + 3\text{FeCl}_3 + 2\text{H}_2\text{O}$. The faintly alkaline solution of the substance (0.1 to 0.2 grm. nitrite) is placed in a round flask closed by a three-holed rubber cork. Through the holes of the cork pass—(1) a tube bent twice at an acute angle, the free end being narrowed to a point which dips into a trough filled with 12 per cent caustic soda; (2) a tube from a Kipp's apparatus generating carbon dioxide which is washed with potassium carbonate solution. This tube reaches nearly to the bottom of the round flask; (3) a separating funnel, which before the experiment is filled up to the cock with pure water. All the air is first expelled by passing a current of carbon dioxide for ten minutes, after which over the end of the bent tube a eudiometer tube filled with 12 per cent caustic soda is placed. Then 10 to 15 c.c. of a 5 per cent potassium iodide solution are introduced into the flask through the separating funnel, and an equal amount of dilute hydrochloric acid. The nitric oxide begins to be evolved at once, and the reaction is hastened first by gentle warming and then by heating until a state of incipient ebullition is reached, a current of carbon dioxide being simultaneously passed through the apparatus so that the last traces of nitric oxide may be expelled. As soon as the volume of gas obtained no longer increases, the eudiometer is removed, well shaken, and transferred to a high cylinder with water, and left for ten minutes. If the nitric acid is to be determined in the residue, a fresh eudiometer filled with caustic soda is brought over the bent tube, and by means of the separating funnel 10 to 20 c.c. of a concentrated strongly acid solution of ferrous chloride in hydrochloric acid is introduced, and the experiment is then concluded as in Spiegel's modification of Schulze and Tiemann's method (*Berichte*, 1890, xxiii., 1361). The advantages of this method are—(1) it takes very little time—at the most an hour and a-half from beginning to end, if the apparatus is prepared beforehand—(2) the determination of both acids is performed on the same quantity of substance; and (3) both acids are determined directly, thus avoiding errors of indirect methods.

Modifications of Antimony.—Alfred Stock and Werner Siebert.—Like arsenic, antimony exists in three forms, yellow, black, and metallic-grey. The last is the most stable form and the only one existing in nature. Pure black antimony may be prepared by transforming the yellow form, by the action of oxygen or air on liquid antimony hydride at temperatures above -90° , and by rapid cooling of the vapours of ordinary antimony. This last operation may be performed in the apparatus devised by the authors for the conversion of black arsenic into the yellow modification (*Berichte*, 1904, xxvii., 4572). The sublimation of the antimony must be effected at the lowest possible temperature, otherwise a grey instead of a black sublimate is obtained. For the second method of preparation of black

antimony, small bubbles of oxygen are introduced into liquid antimony hydride at about -40° . After evaporating off the antimony hydride, the fine velvety black powder is freed from oxide by treating it with hydrochloric acid, washed with alcohol and ether, and dried *in vacuo*. The third method of formation consists in warming the yellow form above -90° , or exposing it to the action of light at lower temperatures; it is of no practical importance. The black antimony thus obtained seems to be always amorphous, no crystallisation ever having been observed. If ordinary antimony is heated in an exhausted glass tube, at first a thin mirror of the black variety forms at some distance from the heated part, and soon, between this and the ordinary antimony, a metallic-grey deposit is produced. This shows that black antimony is more easily volatilised than metallic antimony. The density of the black variety is 5.3. It is chemically more active than the grey variety; it oxidises in air at the ordinary temperature, and when finely divided antimony, prepared from oxygen and liquid antimony hydride, is left at the ordinary temperature in contact with air it often ignites. If when it is being prepared the oxygen is allowed to act upon it too long a grey layer of oxide is formed on it; this may be removed by washing with hydrochloric acid. Black antimony, when warmed in absence of air, yields the metallic modification, an alteration taking place in appearance and density. The transformation takes place rapidly at 400° , and slowly on boiling with water. The black modification appears to be labile at ordinary temperatures, and the metallic form is stable. Antimony, like arsenic, is monotropic. The three elements, antimony, arsenic, and phosphorus, exhibit the interesting phenomenon that at the ordinary temperature the metallic form is stable in the case of the first, the black amorphous variety in the case of the second, and the yellow form (in absence of air) in the case of the third. When antimony chloride is reduced with aluminium, a black-looking metal is obtained; but in this and other cases it appears that a mixture of black and metallic antimony is formed. The yellow variety has been prepared by leading oxygen into liquid antimony hydride at -90° . On warming the yellow substance pure black antimony is formed. The yellow modification retains a small quantity of antimony hydride mechanically. When solutions of chlorine and antimony hydride react together in liquid ethane at -100° , pure yellow antimony separates out. After filtering and washing with pure liquid ethane (in a red light at -100°) the yellow antimony was dried at the same temperature in the vacuum of the mercury air-pump. It was found to be not perfectly pure, but on warming yielded small quantities of a gas. Yellow antimony is even more unstable than yellow arsenic. Above -90° it soon becomes black in the dark, and the same change occurs at a lower temperature in sunlight. When yellow antimony is warmed with carbon disulphide the liquid turns yellow, although this is not due to the solution of the antimony, as has been supposed, but to the conversion of the yellow into the black variety. A solution of yellow arsenic in carbon disulphide is quite colourless, but begins to turn yellow on standing, and yellow antimony behaves exactly similarly, the yellow liquid being not a true solution, but containing insoluble antimony in the colloidal state. It becomes colourless on filtering. The solubility of yellow antimony in carbon disulphide is very small at low temperatures, and only becomes appreciable at temperatures at which the resulting solution is no longer stable. "Explosive" antimony has been shown by Cohen to contain a modification of antimony which he calls "*a*-antimony," and the explosion is due to the transformation of the *a* into the ordinary variety. Probably "*a*-antimony" is identical with black antimony; to settle the question of its nature the heat of formation of grey antimony from the black variety must be determined.

MEETINGS FOR THE WEEK.

TUE. DAY, Jan. 2 } Royal Institution, 3. (Christmas Lectures,
THURSDAY, " 4 } adapted to a Juvenile Auditory). "Astronomy,"
SATURDAY, " 6 } by Prof. Herbert Hal Turner, D.Sc., F.R.S.

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